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Substituent Effects on the Stereochemistry in the [2 + 2] Photocycloaddition Reaction of Homobenzoquinone Derivative with Variously Substituted Alkenes and Alkynes

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Abstract: Irradiation of a homobenzoquinone derivative with variously substituted alkenes and alkynes gave the [2 + 2] photocycloadducts, tricyclic diones, almost quantitatively as a mixture of regio- and stereoisomers. The preferred regioisomer for all reactions is attributed to the more stable 1,4-biradical intermediate (major addition mode), and the minor isomer is attributed to the less stable biradical (minor addition mode). A radical trapping experiment using benzeneselenol proved the generation of these two regioisomeric biradicals, reflecting the regioselectivity in selenol-free photoreaction. Both biradicals tended to preferentially yield the endo-isomer for the alkenes with smaller substituents such as ethoxy, cyano, and acetoxy groups, but the exo-isomer for the alkenes with larger substituents such as phenyl, carbazolyl, and *tert*-butyl groups. The logarithmic exo/endo ratios were well correlated with a combination of Taft's steric factor E_s and the energy gain ($\Delta E'$) associated with the orbital interactions between the spin centers of 1,4-biradicals. These results were interpreted in terms of Griesbeck's SOC mechanism as well as the possible bond rotation around the armed radical chain. Therefore, it is concluded that a balance of repulsive steric hindrance and the attractive FMO interaction determines the stereochemical course of the [2 + 2] photoaddition of homobenzoquinone derivative with variously substituted alkenes.

Introduction

The [2 + 2] photoaddition of cyclic enones with alkenes is an efficient method for the construction of bicyclic ketones with four-membered rings and is successfully utilized in the synthesis of some polycyclic natural products.[1] Since the early work by Corey on the photoaddition of cyclohexenone with various alkenes in 1964,[2] an enormous number of studies have been devoted to the synthetic and mechanistic features of these photoreactions.[3] According to the generally accepted mechanism, these reactions are thought to proceed through a photoexcitation of enone (occasionally followed by exciplex formation), a rapid intersystem crossing (ISC) to the triplet state, and an addition to alkene to afford the triplet biradical which collapses to the [2 + 2] product or cleaves to the starting components via spin inversion. Usually, these reactions provide several regio- and stereoisomers depending on the substituents of the alkenes and enones. Thus, in viewpoint of the synthetic organic chemistry, it is necessary to elucidate a factor that determines the stereochemistry of the enone-alkene photocycloaddition.

Corey proposed an oriented exciplex formation between the photoexcited enone and the ground-state alkene on the basis of the preferential head-to-tail (HT) adduct for the electron-rich alkene and the head-to-head (HH) for the electron-poor alkene.[2] However, this propensity is not necessarily the case for a wide variety of alkenes. Bauslaugh argued the biradical mechanism with no exciplex in 1970, in which the regiochemistry is dependent on the stability of the 1,4-biradical intermediate.[4]

In contrast to the regiochemistry of the [2 + 2] photocycloaddition, a factor by which the stereochemistry regarding the cis/trans- and exo/endo-selectivity is governed still remains somewhat unclear, although many stereoselective examples are known in a recent review.[5] The [2 + 2] photoaddition occurs in cis-configuration in most cases because of the ring strain.[6] However, some examples of trans-fusion are reported for the electron-rich alkenes and explained by the twisted $\pi\pi^*$ triplet state.[7] The exo/endo-selectivity of the addition mode of the substituted alkenes has also attracted much attention because the product stereochemistry can be taken as a powerful tool in the elucidation of many mechanistic problems on the cyclization

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(1) (a) Weedon, A. C. In *Synthetic Organic Chemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; Chapter 2. (b) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453.
(2) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.
(3) Schuster, D. I.; Lem, G.; Kaprinidis, N. A. *Chem. Rev.* **1993**, *93*, 3.
(4) Bauslaugh, P. G. *Synthesis* **1970**, 287.
(5) Bach, T. *Synthesis* **1998**, 683.
(6) For example, [2 + 2] photoaddition of a cyclic enone with cyclic alkenes gave cis−transoid−cis adducts: Hatsui, T.; Kitashima, T.; Takeshita, H. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 293.
(7) (a) Bowman, R. M.; Calvo, C.; McCullough, J. J.; Rasmussen, P. W.; Syder, F. F. *J. Org. Chem.* **1972**, *37*, 2084. (b) Schuster, D. I.; Greenberg, M. M.; Nuñez, I. M.; Tucker, P. C. *J. Org. Chem.* **1983**, *48*, 2615. (c) Broeker, J. L.; Eksterowicz, J. E.; Belk, A. J.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 1847.

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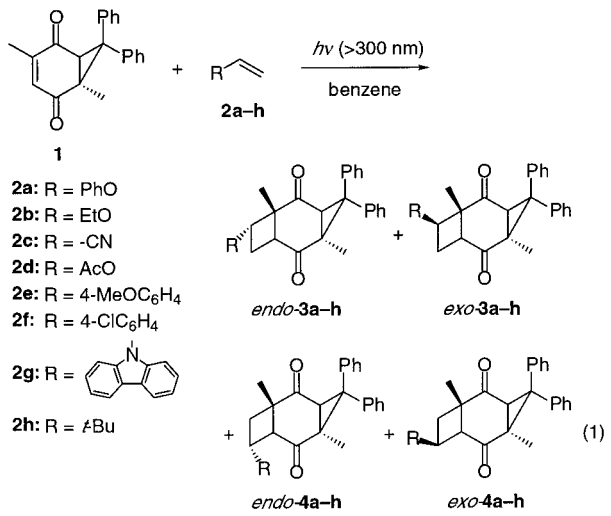
process.[8] Shaik proposed a spin-inversion mechanism in the triplet [$_{\pi}2_s + _{\pi}2_s$] complex,[9] and Sano et al. explained the exo-selectivity in the reaction of β-deuterated styrene with cyclopentenone by assuming the preferential antarafacial addition.[10] Somekawa reasonably rationalized both regio- and stereochemistry in the [2 + 2] photocycloaddition of cyclic enones with alkenes in terms of frontier molecular orbital (FMO) interactions by means of a PM3-CI calculation.[11] Recently, Griesbeck et al.[12] and Abe et al.[13] discussed the exo/endo-selectivity on the Paternò−Büchi reaction of aldehydes with alkenes on the basis of the spin−orbit coupling (SOC) interaction of the 1,4-biradical intermediates, arguing the importance of the distance between two radical centers for the enhanced intersystem crossing (ISC).

We previously reported that the [2 + 2] photoaddition of variously substituted homobenzoquinone derivatives with ethyl vinyl ether gives preferentially endo-adducts irrespective of the substituents and their substitution type.[14] However, we have found that the exo/endo-selectivity is reversed when the alkene substituents are changed from the smaller to the larger ones. In this paper, on the basis of the extended investigation using variously substituted alkenes and alkynes as well as a careful stereochemical analysis of all the possible stereoisomers, we will discuss a factor which controls the regiochemistry and the exo/endo-selectivity of the [2 + 2] photoaddition of homobenzoquinone **1** with alkenes.

Results and Discussion

Photoreaction of Homobenzoquinone 1 with Alkenes 2a−h. Irradiation of homobenzoquinone **1** (30 mM) with a 20-fold excess of variously substituted terminal alkenes **2a−h** was carried out under an argon atmosphere in C_6D_6 solution with a high-pressure mercury lamp through a Pyrex filter (>300 nm) (eq 1).[15] All of the reactions of **1** with **2a−h** gave a regio- and



stereoisomeric mixture of four possible [2 + 2] photoadducts, *endo*- and *exo*-**3**, **4**, in almost quantitative total yields, although the electron-deficient alkenes **2c**, **2d** and the bulky alkenes **2g**, **2h** needed a longer irradiation time (3.5−48 h) (Table 1).

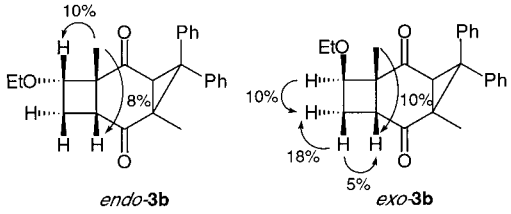
Table 1. Product Distributions in [2 + 2] Photocycloaddition of Homoquinone **1** with Various Alkenes **2a−h**[a]

			yield/%[b]			
2	time/h	conv/%[b]	*endo*-**3**	*exo*-**3**	*endo*-**4**	*exo*-**4**
2a	1	96	62	9	19	6
2b	1	100	69	11	14	6
2c	30	97	71	16	9 (mix)[c]	
2d	3.5	97	53	34	6	3
2e	1	100	12	69	10	8
2f	1	100	12	71	8	9
2g	5[d]	100	4	57	16	22
2h	48	100	tr[e]	90	tr	tr

[a] Irradiation (>300 nm) of **1** (0.03 mmol) with **2** (0.60 mmol) in C_6D_6 (1 mL) under argon atmosphere at room temperature. [b] Determined by ^{1}H NMR on the basis of **1** used. [c] Could not be separated. [d] Five equivalents of **2g** (0.15 mmol) was used. [e] Trace amount (<5%).

The quantum yields for the conversion of **1** (10 mM) with **2b** and **2e** (1 M) were representatively determined to be Φ = 0.15 and 0.24, respectively, by irradiation at λ = 365 nm with potassium ferric(III) trioxalate as an actinometer. The product distributions of these [2 + 2] adducts were determined prior to the usual workup by ^{1}H NMR using an internal standard (1,1,1,2-tetrachloroethane). These photoadducts were preliminary separated by silica gel column chromatography, and then each isomer was isolated by preparative HPLC and/or recrystallization. The tricyclic structures of these regio- and stereoisomers were elaborately determined by IR and ^{13}C and ^{1}H NMR with the aid of differential NOE.[18] The stereochemistry of the main products *exo*-**3e** and *exo*-**3h** was also confirmed by X-ray crystal structure analysis (Figure 1b,c). The relative configuration of all the tricyclic-ring skeletons was identified as cis−transoid−cis, showing the exclusive anti-approach of the alkenes with respect to the cyclopropane ring of homoquinone **1** probably because of the steric hindrance of the endo-phenyl group (Figure 1a). Such a facial selective addition of alkenes was usually found in the photoreaction with α,β-unsaturated

(8) (a) Dilling, W. L.; Tabor, T. E.; Boer, F. P.; North, P. P. *J. Am. Chem. Soc.* **1970**, *92*, 1399. (b) Loutfy, R. O.; De Mayo, P. *Can. J. Chem.* **1972**, *50*, 3465. (c) El-Nabi, H. A. A. *Tetrahedron* **1997**, *53*, 1813.
(9) (a) Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 18. (b) Shaik, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 3184.
(10) Sano, T.; Horiguchi, Y.; Tsuda, Y. *Chem. Pharm. Bull.* **1987**, *35*, 23.
(11) (a) Somekawa, K.; Hara, R.; Kinnami, K.; Muraoka, F.; Suishu, T.; Shimo, T. *Chem. Lett.* **1995**, 407. (b) Suishu, T.; Shimo, T.; Somekawa, K. *Tetrahedron* **1997**, *53*, 3545.
(12) (a) Griesbeck, A. G.; Stadtmüller, S. *J. Am. Chem. Soc.* **1991**, *113*, 6923. (b) Griesbeck, A. G.; Mauder, H.; Stadtmüller, S. *Acc. Chem. Res.* **1994**, *27*, 70. (c) Griesbeck, A. G.; Buhr, S.; Fiege, M.; Schmickler, H.; Lex, J. *J. Org. Chem.* **1998**, *63*, 3847.
(13) (a) Abe, M.; Torii, E.; Nojima, M. *J. Org. Chem.* **2000**, *65*, 3426. (b) Abe, M.; Fujimoto, K.; Nojima, M. *J. Am. Chem. Soc.* **2000**, *122*, 4005.
(14) Kokubo, K.; Nakajima, Y.; Iijima, K.; Yamaguchi, H.; Kawamoto, T.; Oshima, T. *J. Org. Chem.* **2000**, *65*, 3371.
(15) The UV absorption spectra of homobenzoquinone **1** (1 mM) in acetonitrile showed a characteristic absorption (λ_{max} = 372 nm (ϵ = 207)) assignable to the n−π* transition, but no spectral change was observed by addition of excess of ethyl vinyl ether **2b** (20 equiv). Because no fluorescence spectrum of **1** and no exciplex emission in the presence of **2b** were also observed, the photoexcited **1** suffers the efficient intersystem crossing to the $\pi-\pi$* excited triplet state according to the El-Sayed rule.[16] The triplet state of **1** seems to be somewhat twisted on the C=C double bond because such a conformational deformation is well known for the $\pi-\pi$* triplet state of enone.[17]
(16) (a) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834. (b) See also: Dauben, W. G.; Hecht, S. *J. Org. Chem.* **1998**, *63*, 6102.
(17) Broeker, J. L.; Eksterowicz, J. E.; Belk, A. J.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 1847.
(18) Examples of differential NOE data:



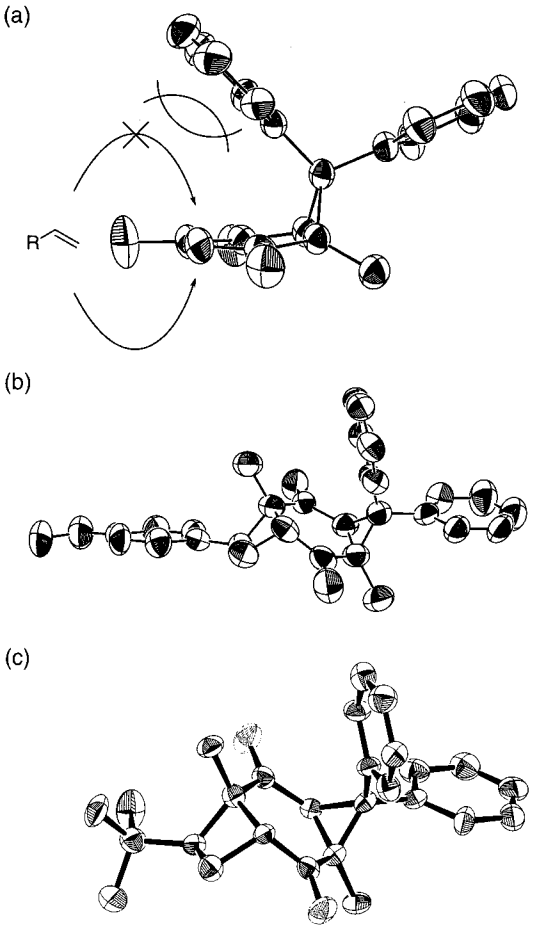


Figure 1. ORTEP drawings of (a) homobenzoquinone **1**, substrate; (b) *exo*-**3e** and (c) *exo*-**3h**, the main products of the photoreaction of **1** with 4-methoxystyrene **2e** or 3,3-dimethyl-1-butene **2h**, respectively.

bicyclic enones. Wiesner proposed the pyramidalization of the β-carbon of the excited state by which the initial addition of alkenes was restricted in one side of the cyclic enones.[19]

In all of the reactions, the products *endo*- and *exo*-**3** may be derived from the same biradical intermediate, and also their regioisomers *endo*- and *exo*-**4** may be derived from another biradical (vide infra). The sum of *endo*- and *exo*-**3** exceeded that of *endo*- and *exo*-**4**. It is also noted that the major addition mode preferentially provides the *endo*-**3** for the alkenes **2a**−**d** with smaller substituents, but the *exo*-**3** for the alkenes **2e**−**h** with aromatic and/or bulky substituents. Similar substituent effects on the exo/endo-selectivity were also observed for the minor addition mode giving **4**, although the effects were not so appreciable (we will discuss these substituent effects further in a later section).

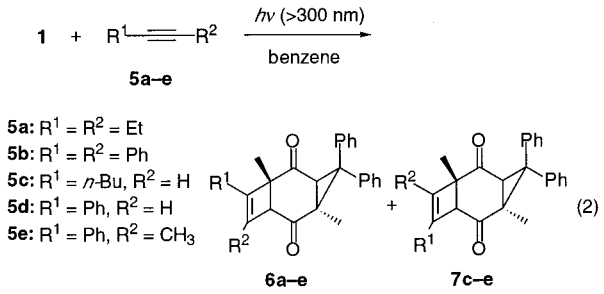
Photoreaction of Homobenzoquinone 1 with Alkynes 5a−**e.** We also conducted the photoreaction of **1** with alkynes **5a**−**e** to know the effects of changing carbon hybridization on the regiochemistry of the possible [2 + 2] adducts.[20] The predicted 1,4-biradical has one of the unpaired electrons in the rehybridized sp^2 orbital of the intrinsic alkyne carbon atom (σ-radical), the so-called vinyl radical, while the corresponding biradical from alkene locates the relevant spin density in the remaining p-orbital of the sp^2-hybridized carbon atom (π-radical).

Table 2. Product Distributions in [2 + 2] Photocycloaddition of Homoquinone **1** with Alkynes **5a**−**e**[a]

			yield/%[b]	
5	time/h	conv/%[b]	**6**	**7**
5a	30[c]	90	88	
5b	48[d]	90	81	
5c	26	93	36	*e*
5d	23	77	57	7
5e	42	90	83	7

[a] Irradiation (>300 nm) of **1** (0.03 mmol) with **5** (0.12 mmol) in C_6D_6 (1 mL) under argon atmosphere at room temperature. [b] Determined by ^{1}H NMR on the basis of **5** used. [c] Ten equivalents of **5a** (0.30 mmol) was used. [d] Three equivalents of **5b** (0.09 mmol) was used. [e] Not detected.

All of the alkynes used added to the C═C double bond of homobenzoquinone **1** to give the desired [2 + 2] adducts **6** and **7** in high yields except 1-hexyne **5c** (36%) (eq 2, Table 2).

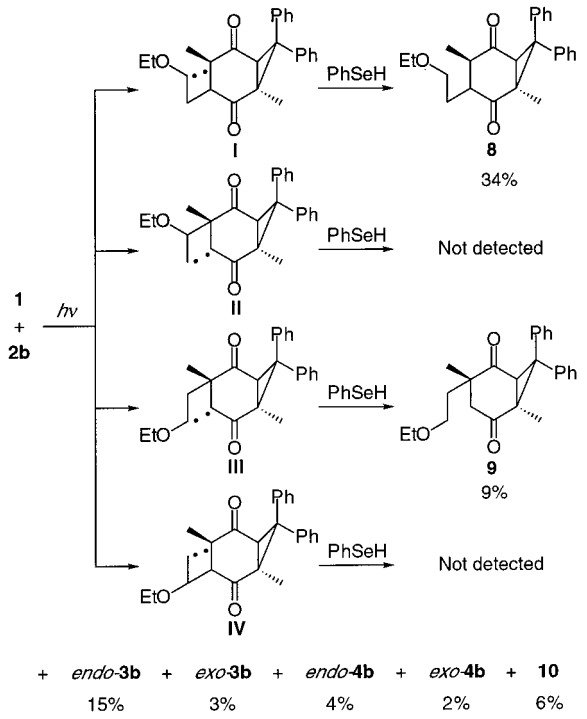


The relative stereochemistry of tricyclic rings was identified as cis−transoid−cis by ^{1}H NMR which exhibited the shielded high-field chemical shift of the bridgehead methyl group (0.4−0.7 ppm in $CDCl_3$) by the overhanged phenyl group as well as the observed NOE enhancement with the adjacent methine proton (13−16%). The regiochemistry of **6e** was also deduced from the differential NOE measurement. Unsymmetrical alkynes **5c**−**e** gave selectively the adducts **6c**−**e** derived from the more stable biradicals; 1-hexyne **5c** yielded only **6c**. The internal alkyne methylphenylacetylene **5e** provided the higher regioisomer ratio (**6e**/**7e** = 12) as compared with the terminal phenylacetylene **5d** (=8.1). The higher regioselectivity of **5e** may be explained by the lower reactivity toward the excited **1** on account of the steric hindrance of the terminal methyl group. These regioisomer ratios are about 2 times higher than those of the corresponding alkenes such as *p*-chloro- and *p*-methoxystyrenes (**3**/**4** = 4.5−4.9) (Table 1). This can be also accounted for by considering the lower reactivity of alkynes as compared to that of alkenes. Indeed, the **5d** and **5e** required over 20−40-fold longer irradiation times for the practical reaction, while the *p*-chloro- and *p*-methoxystyrenes completed the [2 + 2] addition within 1 h. As a result, the photoaddition of **1** with alkenes and alkynes preferentially gave the [2 + 2] adducts via the stable 1,4-biradicals irrespective of the nature of the radical center, that is, π- and σ-radical.

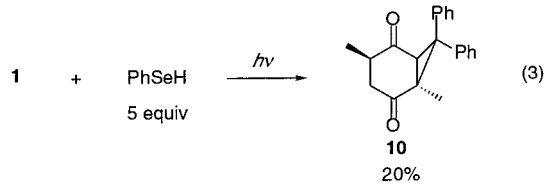
(19) (a) Wiesner, K. *Tetrahedron* **1975**, *31*, 1655. (b) Marini-Bettòlo, G.; Sahoo, S. P.; Poulton, G. A.; Tsai, T. Y. R.; Wiesner, K. *Tetrahedron* **1980**, *36*, 719. (c) Bourgin, D.; Büchel, R.; Gerber, P.; Keese, R. *Tetrahedron Lett.* **1994**, *35*, 3267.

(20) Photoreaction of quinones with alkynes, for example: (a) Zimmermann, H. E.; Craft, L. *Tetrahedron Lett.* **1966**, 4783. (b) Bryce-Smith, D.; Fray, G. I.; Gilbert, A. *Tetrahedron Lett.* **1964**, 2137. (c) Farid, S.; Kothe, W.; Pfundt, G. *Tetrahedron Lett.* **1968**, 4147. (d) Pappas, S. P.; Portnoy, N. A. *J. Org. Chem.* **1968**, *33*, 2200. (e) Kuehne, M. E.; Linde, H. *J. Org. Chem.* **1972**, *37*, 4031. (f) Kim, A. R.; Mah, Y. J.; Kim, S. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 1295.

Scheme 1



Trapping Experiment of Intermediate 1,4-Biradical with Benzeneselenol. To confirm the generation of regioisomeric biradical species, a combination of homobenzoquinone **1** and **2b** was irradiated (>300 nm) with 5 equiv of PhSeH as a radical scavenger in benzene solution under argon atmosphere for 3 h. The radical trapped products **8** and **9** were obtained in 34 and 9% yields, respectively, along with the usual [2 + 2] photoadducts *endo*- and *exo*-**3b**, **4b** and the hydrogenated **10** (6%) (Scheme 1). The compound **10** seems to arise from the direct reaction of PhSeH with the excited **1**, because the similar irradiation in the absence of **2b** exclusively gave **10** as a sole product in 20% conversion (eq 3), but this hydrogenation was completely inhibited in the dark.



The considerable formation of **8** and **9**, taken as direct evidence for the intermediacy of biradicals **I** and **III**, is also suggestive of the triplet multiplicity for these intermediates rather than the short-lived singlet ones. Some triplet 1,4-biradicals derived from cyclic enones and alkenes have been estimated to have a lifetime on the order of 50 ns which should be sufficient for the conformational equilibration.[21] Actually, in the photocycloaddition of 2-methylpropene with some cyclopentenones, the triplet 1,4-biradicals were quantitatively trapped by H_2Se as a hydrogen atom donor.[22c] On the contrary, the absence of the trapping products from possible **II** and **IV** indicates that the initial bond formation between the excited **1** and **2b** exclusively occurs at the less-hindered β-position of **2b**, yielding the more stable secondary radical terminus.

It is also noted that the relative yields of the [2 + 2] adducts, *endo*- and *exo*-**3b**, **4b** (15, 3, 4, and 2% yields, respectively), are roughly comparable to those in the selenol-free reaction (69, 11, 14, and 6%, Table 1). The formation of these untrapped products means that the singlet biradicals can be competitively generated in the conformations suitable for the SOC (vide infra). Furthermore, the regioisomeric product ratio (**8**/**9** = 3.8) is approximately equivalent to that of the [2 + 2] adducts (**3b**/**4b** = 4). These observations demonstrate that both of the biradicals **I** and **III** collapse essentially in the same rate ratio in the competitive intramolecular cyclization via ISC and the intermolecular hydrogen abstraction from PhSeH in the trapping experiment. Thus, our reaction system is significantly different from Weedon's [2 + 2] photoreaction of cyclopentenone with **2b**, in which the two regioisomeric 1,4-biradicals were trapped in almost the same amount by H_2Se, although their selenide-free reaction provided about 3 times more HT adduct than the HH adduct.[22] The present trapping experiment with PhSeH apparently manifested our previous arguments that the regiochemistry of the [2 + 2] photoreaction of homobenzoquinone derivatives with **2b** is much dependent on the relative stability of 1,4-biradical intermediates, and not on the appreciable biradical dissociation to the starting substrates.[14]

Does the Photoinduced Electron Transfer (PET) Take Place in the Present Reactions? Considering that the photoreaction of the analogous bromohomobenzoquinone derivative with amine and arene compounds proceeds through an electron transfer,[23] we attempted to trap a possible cation radical[24] by methanol in the [2 + 2] photocycloaddition of **1** with such electron-rich alkenes as 4-methoxystyrene **2e** (E_{ox} = 1.4 V vs SCE),[25] 4-chlorostyrene **2f** (2.0),[25] and 9-vinylcarbazole **2g** (1.2).[26] The photoreaction of **1** (30 mM) with 5 equiv of **2e**, **2f**, and **2g** in benzene in the presence of a 100-fold excess of methanol (ca. 10 vol %) for 4−5 h was found to give no methanol adducts but yielded the usual [2 + 2] adducts in almost the same product distributions as the methanol-free reaction (Table 3). Unfortunately, the lack of the reliable triplet energy of **1** does not allow the estimation of the free energy change of electron transfer (ΔG_{ET}) by the Rehm−Weller equation.[27]

Contrary to **1**, a preliminary photoirradiation of the stronger acceptor chloranil (30 mM) with **2g** (5 equiv) in benzene for 4 h in the presence of methanol (10 vol %) resulted in the quantitative formation of Markovnikov-type methanol adduct **11** without any consumption of chloranil (Scheme 2). Because the chloranil reaction in the dark did not afford **11**, it is obvious that the excited chloranil abstracts an electron from the donor **2g** to produce its radical cation **V**. The intermediate **V** seems to degrade to **11** via a nucleophilic attack of methanol followed

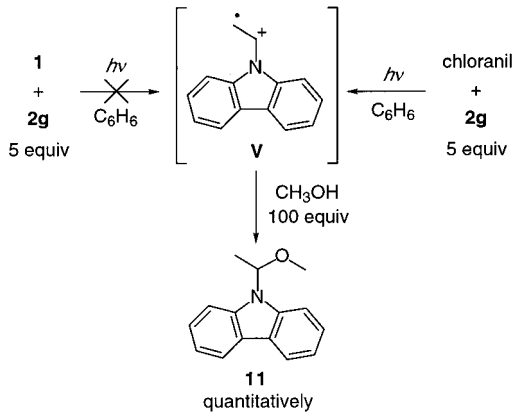
(21) (a) Rudolph, A.; Weedon, A. C. *Can. J. Chem.* **1990**, *68*, 1590. (b) Kaprinidis, N. A.; Lem, G.; Courtney, S. H.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 3324.
(22) (a) Hastings, D. J.; Weedon, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 8525. (b) Andrew, D.; Hastings, D. J.; Weedon, A. C. *J. Am. Chem. Soc.* **1994**, *116*, 10870. (c) Andrew, D.; Weedon, A. C. *J. Am. Chem. Soc.* **1995**, *117*, 5647.
(23) (a) Moriwaki, H.; Oshima, T.; Nagai, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2517. (b) Moriwaki, H.; Matsumoto, T.; Nagai, T.; Oshima, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1461. (c) Moriwaki, H.; Fukushima, K.; Nagai, T.; Oshima, T. *Chem. Commun.* **1996**, 495.
(24) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99.
(25) Kojima, M.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 521.
(26) Fox, M. A., Chanon, M., Eds. *Photoinduced Electron Transfer*, part C; Elsevier: Amsterdam, 1988; p 5.
(27) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

Table 3. Solvent Effects on the [2 + 2] Photocycloaddition of Homoquinone **1** with Alkenes **2e**−**g**[a]

					yield/%[b]			
entry	**2**	solvent	time/h	conv/%[b]	*endo*-**3**	*exo*-**3**	*endo*-**4**	*exo*-**4**
1	**2e**	C_6D_6[c]	1	100	12	69	10	8
2	**2e**	C_6H_6/CH_3OH[d]	4	91	9	66	11	5
3	**2f**	C_6D_6[c]	1	100	12	71	8	9
4	**2f**	C_6H_6/CH_3OH[d]	4	95	12	65	7	11
5	**2g**	C_6D_6	5	100	4	57	16	22
6	**2g**	C_6H_6/CH_3Oh[d]	5	97	2	65	16	15

[a] Irradiation (>300 nm) of **1** (0.03 mmol) with **2** (0.15 mmol) in solvent (1 mL) under argon atmosphere at room temperature. [b] Determined by ^{1}H NMR on the basis of **1** used. [c] Twenty equivalents of **2** (0.6 mmol) was used. [d] In the presence of CH_3OH (3 mmol).

Scheme 2



by a back electron transfer from the radical anion of **1** and a proton migration.

Coupled with the negligible solvent effects on the product distributions (Table 3), the absence of methanol adduct in the above trapping experiments strongly suggests that the 1,4-biradical is the actual intermediate for the [2 + 2] adducts. However, the possibility that the 1,4-biradical is immediately formed by the collapse of the radical ion pair derived from the PET between the excited **1** and the most probable 9-vinylcarbazole **2g** cannot be ruled out at the present stage.

Exo/Endo-Selectivity in [2 + 2] Photocycloaddition of Homobenzoquinone 1 with Alkenes. In the major addition mode giving **3**, the alkenes **2a**−**d** with relatively smaller substituents (R = PhO, EtO, CN, AcO) preferentially gave the endo-isomers regardless of the electron-withdrawing or electron-releasing ability of the substituents, while the bulky *p*-anisyl-, *p*-chlorophenyl-, carbazolyl-, and *tert*-butyl-substituted alkenes **2e**−**h** reversely provided the exo-isomers preferentially (Table 1). Here, we discriminate between the smaller and the larger substituents according to Taft's steric parameters;[28] that is, PhO ($E_s = -0.55$), EtO (−0.55), CN (−0.51), AcO (−0.55), *p*-$CH_3OC_6H_4$ and *p*-ClC_6H_4 (−1.01),[29] *t*-Bu (−2.78). Thus, the exo/endo ratios increased from 0.15 to >18 in going from **2a** to **2h** (Table 4). The same trend appeared in the minor addition mode giving **4**, although the variation of the exo/endo ratios only ranges from 0.32 to 1.4 from **2a** to **2g**.

(28) Fujita, T.; Nishioka, T. *Prog. Phys. Org. Chem.* **1976**, *12*, 49.
(29) The E_s for **2e** and **2f** was not reported but substituted by that of the parent phenyl group (−1.01).

Table 4. Exo/Endo Ratios in [2 + 2] Photocycloaddition of Homoquinone **1** with Alkenes **2a**−**h**, Calculated MO Coefficients (C_a), and Energies (e_a/eV) for Intermediate Alkene Radical Termini and Taft's Steric Parameter E_s

	exo/endo ratio				ΔE′/eV		
2	**3**	**4**	C_a[a]	e_a/eV[a]	**3**	**4**	E_s[b]
2a	0.15	0.32	0.74	−8.59	0.32	0.25	−0.55
2b	0.16	0.43	0.99	−8.58	0.57	0.46	−0.55
2c	0.23		0.97	−10.57	1.02	4.24	−0.51
2d	0.64	0.50	0.99	−9.68	3.82	1.17	−0.55
2e	5.8	0.80	0.65	−7.55	0.14	0.12	−1.01[c]
2f	5.9	1.1	0.74	−8.29	0.26	0.22	−1.01[c]
2g	14	1.4	0.47	−7.35	0.07	0.06	*d*
2h	>18		1.07	−8.93	0.90	0.65	−2.78

[a] Calculated at the UHF/6-31G* level of theory for the corresponding monohydrogenated radicals. Calculated MO coefficients (C_b) and energies (e_b) for intermediate homoquinone radical termini are 0.87 and −9.88 eV for **3** and 0.91 and −10.38 eV for **4**, respectively. [b] Taft's steric parameter for the alkene substituents. [c] Using the value for phenyl group. [d] Not reported.

What are the factors that govern the exo/endo-selectivity in the present [2 + 2] photocycloaddition? In the previous paper,[14] we have rationalized the endo-selectivity in the [2 + 2] photocycloaddition of ethyl vinyl ether **2b** with variously substituted homobenzoquinone derivatives by resting on Griesbeck's SOC mechanism devoted for the Paternò−Büchi reaction of aldehydes and alkenes[12] as well as the [2 + 2] photocycloaddition reaction of cyclic enones with alkenes.[30] According to this concept, it is necessary to orient the two singly occupied orbitals of triplet 1,4-biradicals perpendicularly from each other to maximize SOC as represented for the conformers **A** and **B** responsible for the major addition mode (Scheme 3).[31] Here, we dismiss the corresponding less stable conformers in which the substituent R is pointing to the homoquinone moiety because of the more steric interactions.

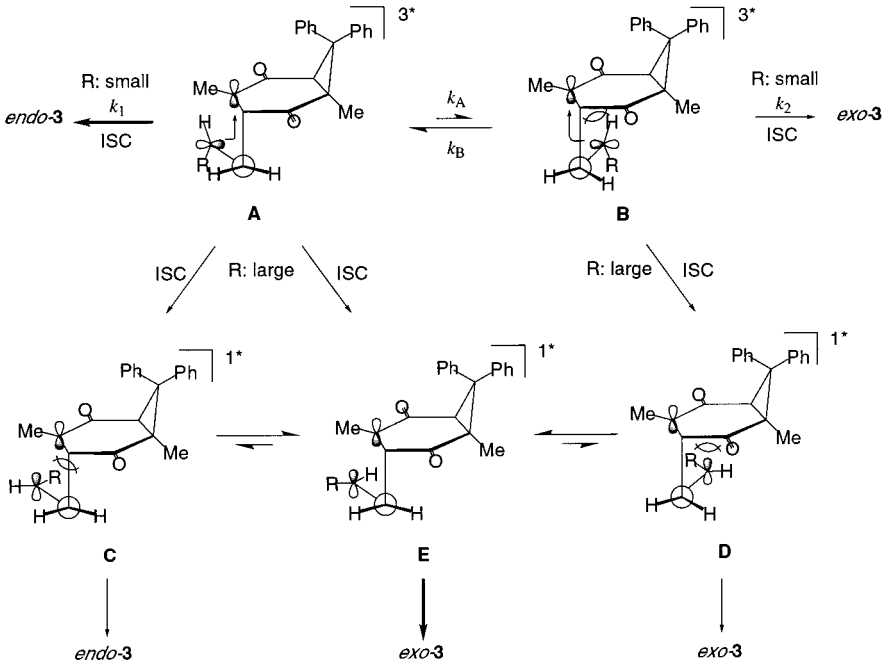
The conformer **A** is more populated than the conformer **B** because the latter suffers the more unfavorable double gauche interactions because of the inward-directed armed-chain. If **A** and **B** are in rapid equilibrium (i.e., k_A, $k_B \gg k_1$, k_2), the Curtin−Hammett principle[32] predicts the endo-selectivity provided that **A** has a smaller standard Gibbs free energy of the transition state for *endo*-**3** than does **B** for *exo*-**3**. In this case, the product ratio, *endo*-**3**/*exo*-**3**, can be expressed by eq 4, where $\Delta G^{\neq}$ ($=G^{\neq}_A - G^{\neq}_B$) is the difference in the free energies of the transition states for the two products.

$$\textit{endo}\text{-}\mathbf{3}/\textit{exo}\text{-}\mathbf{3} = e^{-\Delta G^{\neq}/RT} \quad (4)$$

On the basis of the above conformational considerations, the transition state of the orthogonal overlapping of the spin-orbitals for the SOC seems to be less hindered for **A** as compared with **B** ($k_1 > k_2$). In contrast to this, the case that the equilibration between **A** and **B** will occur very slowly (i.e., k_A, $k_B \ll k_1$, k_2) will simply relate the product ratio, *endo*-**3**/*exo*-**3**, to the conformer ratio **A**/**B**. However, this situation is less promising because the rate constant for the C−C bond rotation in the

(30) Kelly, J. F. D.; Kelly, J. M.; McMurry, T. B. H. *J. Chem. Soc., Perkin Trans. 2* **1999**, 1933.
(31) (a) Zimmerman, H. E.; Kutateladze, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 249. (b) Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3568. (c) Havlas, Z.; Downing, J. W.; Michl, J. *J. Phys. Chem. A* **1998**, *102*, 5681. (d) Kutateladze, A. G. *J. Am. Chem. Soc.* **2001**, *123*, 9279.
(32) (a) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111. (b) Gold, V. *Pure Appl. Chem.* **1983**, *55*, 1281. (c) Seeman, J. I. *Chem. Rev.* **1983**, *83*, . (d) Seeman, J. I. *J. Chem. Educ.* **1986**, *63*, 42.

Scheme 3



ethane derivatives is on the order of 10^{10-12} s^{-1}, while the rate constant for the ISC of carbon-chained triplet 1,4-radicals is known to be much slower (10^{6-8} s^{-1}).[13b] Thus, the Curtin−Hammett treatment can well explain the endo-selectivity for the alkenes **2a**−**d** with relatively smaller substituents.

Contrary to the endo-selective alkenes, the exo-selective ones with bulky substituents would satisfy their stereochemical outcome if it were true that the conformer **B** is more stable and more rapidly collapses to *exo*-**3** than does the conformer **A** to *endo*-**3**. In fact, the methyl substitution at the spin center like in **B** leads to the inversion of the intrinsic endo-selectivity as found for the Paternò−Büchi reactions of benzaldehyde with cyclopentene/1-methylcyclopentene, although the similar reactions with six-membered ring cyclohexene/1-methylcyclohexene still show the endo-selectivity.[12a] However, the reverse equilibration is hard to conceive because the bulky substituent R should be pointing away from the rest of the molecule in both conformers **A** and **B** as is the smaller substituent. Furthermore, this sophisticated interpretation cannot fulfill the exo-selectivity in the minor addition mode for alkenes **2f** and **2g** because the relevant spin centers have no methyl substituent.

Accordingly, the stereochemistry for bulky alkenes calls for some modification of the Griesbeck model. We would like to explain the exo-selectivity in terms of the occurrence of some C−C bond rotation around the armed radical chain prior to the ring-closure as well as the through-space interactions of spin-delocalized orbitals. Therefore, the stereochemical results for the bulky **2e**−**h** can be rationalized by the following two reasons. First, though only the case for the highly conjugated substituents such as the phenyl and carbazolyl group, the less favorable conformer **B** enables itself to bring about the more enhanced SOC to give the exo-isomer because of the shorter through-space distance between the spin-delocalized aromatic nuclei and the facing spin-conjugated α-carbonyl group. Such an enhancement of ISC by favorable spin−spin interaction was addressed by Griesbeck et al. for the exo-selectivity in the Paternò−Büchi reaction of benzaldehyde with 1,3-cycloalkadienes (furan, cyclopentadiene, and 1,3-cyclohexadiene), in which the spin-delocalized benzylic and allylic radical termini come close to interacting with each other.[12] Furthermore, they observed the switchover in the exo/endo-selectivity when extended to the nonconjugated dihydrofuran in which the reverted endo-selectivity was attributed to the loss of the favorable spin−spin interactions. The spin delocalization also resulted in the elongation of the lifetime of singlet 1,4-biradical so as to increase the chance of possible rotation around the armed radical chain. However, this explanation based on the spin delocalization cannot fold for the less conjugated *tert*-butyl-substituted **2h**. Next is the consideration of substantial steric repulsion in the radical coupling step of the singlet 1,4-biradical derived from SOC, resorting to the assumption that the rotation or torque of the armed radical chain is allowed in competition with the radical collapse. This explanation predicts the intervention of the ISC pathway from the conformer **A** to **C** and **E**, and from **B** to **D** as well as the rapid equilibration between the conformers **C**, **E**, and **D**. Among these singlet conformers, **E** is expected to be most populated and play an important role in the exo-selectivity for the bulky **2e**−**h** because of the fewer steric interactions in the ground state as well as in the radical coupling step to *exo*-**3**, that is, the lowest Gibbs free energy of the transition state (vide supra).

Besides the steric effects in the radical coupling, we must consider the attractive orbital interactions between the spin-orbitals, because the favorable orbital overlapping leads to the more rapid ring-closure in competition with the C−C bond rotation. According to the Klopman[33] and Salem[34] equation as well as the FMO theory, the energy (ΔE) gained in orbital interactions is inversely proportional to the energy difference $|e_a - e_b|$ of the SOMOs as shown in eq 5.

$$\Delta E = \frac{2(C_a C_b \beta_{ab})^2}{|e_a - e_b|} = \text{constant} \times \frac{(C_a C_b)^2}{|e_a - e_b|} \qquad (5)$$

The products C_aC_b denote the overlap of MO coefficients of

(33) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

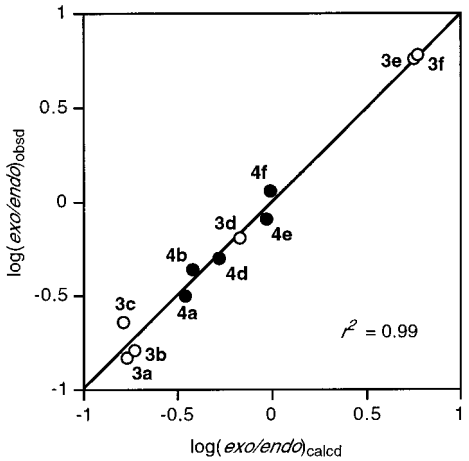


Figure 2. Plots of $\log(\text{exo/endo})_{\text{obsd}}$ vs $\log(\text{exo/endo})_{\text{calcd}}$ according to eq 6 for **3** (○) and to eq 7 for **4** (●).

interacting atomic orbitals. The term β_{ab} is the resonance integral that converts the efficiency of overlap to the energy units. The MO coefficients (C_a and C_b) and SOMO energies (e_a and e_b) of alkene and homoquinone moieties were separately calculated by the ab initio method at the UHF/6-31G* level of theory[35] for the respective monohydrogenated model radicals (Table 4). Although the resonance integral β depends on the distance between the interacting orbitals, it can be approximated to be identical for the comparison of reactivity sequences in a series of reactions (e.g., substituent variation). Thus, the ΔE values are approximately proportional to the β-deleted quotient $(C_aC_b)^2/(|e_a - e_b|)$, which we rewrite as $\Delta E'$ for simplicity to use as a parameter (vide infra). The $\Delta E'$ values are also listed in Table 4 along with Taft's E_s parameter.

To assess the contributions of the above two parameters to the stereochemistry, we attempted to correlate the logarithmic exo/endo ratios with Taft's E_s parameters and with the $\Delta E'$ values. We employed six substituents (R = PhO, EtO, CN, AcO, *p*-$CH_3OC_6H_4$, *p*-ClC_6H_4), for which both the reliable exo/endo ratios and E_s were obtained. A preliminary correlation of log(exo/endo) with the E_s yielded fairly good results: $\log(\text{exo/endo}) = -2.94E_s - 2.20$ ($r^2 = 0.91$, $n = 6$) for the adducts **3**, and $-0.80E_s - 0.83$ ($r^2 = 0.84$, $n = 5$) for the adducts **4**, respectively. A similar treatment with $\Delta E'$ was found to be unsuccessful: $\log(\text{exo/endo}) = -0.086\Delta E' - 0.069$ ($r^2 = 0.026$, $n = 6$) for the adducts **3**, and $-0.151\Delta E' - 0.176$ ($r^2 = 0.085$, $n = 5$) for the adducts **4**, respectively. Thus, the steric hindrance is much more important than the orbital interactions, especially on the major addition mode. However, the two-parameter treatment considerably improved the regression (eqs 6 and 7) and provided excellent linearity through the origin with sufficient correlation coefficients (Figure 2).

$$\log(\text{exo/endo}) = -3.38E_s + 0.17\Delta E' - 2.69 \quad (r^2 = 0.99,\ n = 6 \text{ for } \mathbf{3}) \quad (6)$$

$$\log(\text{exo/endo}) = -0.99E_s + 0.20\Delta E' - 1.06 \quad (r^2 = 0.93,\ n = 5 \text{ for } \mathbf{4}) \quad (7)$$

A comparison of eqs 6 and 7 apparently indicates that the exo/endo ratios increase with the increasing substituent bulk (i.e., increasing negative E_s) and decrease with the increasing orbital interactions (i.e., increasing negative $\Delta E'$). The percent contributions of these parameters are 77 (E_s) and 23% ($\Delta E'$) for **3**, and 75 (E_s) and 25% ($\Delta E'$) for **4**, respectively.[36] The slightly higher efficiency of E_s for **3** is in harmony with the additional steric hindrance because of the presence of the methyl substituent at the spin center.

As a result, the stereochemistry of the present [2 + 2] photoaddition can be rationalized by considering a balance between the conformational equilibration of the triplet 1,4-biradical intermediates, the SOC associated with the spatially favorable orientation of the spin-orbitals, and the significant steric effects in the ring-closure of the singlet 1,4-biradicals.

Finally, we can delineate that the present 1,4-biradical must be more stabilized by the proper substituents in the ground state than in the transition state for the C−C bond formation. A quantity called the radical stabilization energy (RSE) may be defined to relate the stability of substituted carbon radicals to the methyl radical.[37] The averages of the RSE values derived by the several methods for the radicals of the type Z-CH_2• are (Z, RSE in kJ mol^{-1}) H, 0; CH_3O, 4.5; PhO, 4.9; CN, 8.6; Ph, 11.2.[38] On the basis of these numerical values as well as the well-known π-type conjugation, one can imagine that the aromatic substituents and CN as well as AcO would somewhat retard the radical coupling process and consequently contribute to the increment of the exo-adducts by way of the bond rotation.

Conclusions

The [2 + 2] photocycloadditions of homoquinone **1** with variously substituted alkenes **2** and alkynes **5** gave regio- and stereoselectively tricyclic diones, *endo*- and *exo*-**3**, **4**, and **6** and **7**, in almost quantitative yields. The regiochemically preferred addition mode was characterized by the more stable 1,4-biradical intermediates in both reactions with alkenes and alkynes. The trapping experiment using PhSeH for the system of **1** and ethyl vinyl ether **2b** proved the formation of two regioisomeric triplet 1,4-biradical intermediates, reflecting the **3**/**4** ratio in the selenol-free [2 + 2] photoadducts. These results indicate that the regiochemistry is mainly dependent on the stability of the 1,4-biradical intermediates. A failure of the trapping experiment with methanol and the negligible solvent effects on product distributions seem to rule out a possible photoinduced electron transfer (PET) mechanism.

With respect to the stereoselectivity, the alkenes with relatively smaller substituents such as EtO, CN, AcO preferentially gave the endo-adducts according to Griesbeck's SOC mechanism, while exo-selectivity for the alkenes with larger substituents such as aromatic and *tert*-butyl groups was rationalized by the intervention of a possible C−C bond rotation of the singlet 1,4-biradical chain. It was also found that the

(34) (a) Salem, L. *J. Am. Chem. Soc*. **1968**, *90*, 543. (b) Salem, L. *J. Am. Chem. Soc*. **1968**, *90*, 553.

(35) (a) Calculation by using PC Spartan Pro software: Wave function Inc., 18401 Von Karman Ave., Suite 370, Irvine, CA 92612. (b) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(36) Snedecor, G. W.; Cochran, W. G. *Statistical Methods*, 6th ed.; Iowa State University Press: Ames, 1967.

(37) (a) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X. *J. Am. Chem. Soc*. **1991**, *113*, 9790 and references therein. (b) Sustmann, R.; Korth, H.-G. *Adv. Phys. Org. Chem*. **1990**, *26*, 131. (c) Bordwell, F. G.; Zhang, X. M.; Alnajjar, M. S. *J. Am. Chem. Soc*. **1992**, *114*, 7623.

(38) Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; D. Reidel Publishing Co.: Boston, 1986; pp 1−48.

logarithmic exo/endo ratios are well expressed by a two-parameter regression using the steric parameter E_s and the energy gain ($\Delta E'$) associated with the FMO interactions of 1,4-biradical termini. This means the exo/endo-selectivity is governed by the balance between the steric effects (major) and the orbital interactions (minor) at the stage of ring-closure of the biradical intermediate.

Experimental Section

The ^{1}H and ^{13}C NMR spectra were recorded at 270 and 68 MHz, respectively. Photoreactions were carried out under an argon atmosphere in a Pyrex tube with a high-pressure 300 W mercury lamp (Eikohsha EHB W1-300). Quantum yield measurements were performed at 365 nm using an ultrahigh-pressure 500 W mercury lamp (Wacom BMO-500D1) with glass filters (Corning 7-37 and Toshiba UV-35) and a $NiSO_4$ solution filter. Alkenes and alkynes used were all commercially available and were purified by distillation or recrystallization. All deuterated solvents and benzeneselenol were used as purchased. Benzene for preparative runs was refluxed over sodium and fractionated. Homoquinone **1** was synthesized by 1,3-dipolar addition of diphenyldiazomethane to 2,5-dimethylbenzoquinone as previously reported.[14]

General Procedure for Photoreaction of Homoquinone 1 with Alkenes 2a−g and Alkynes 5a−e. A mixture of **1** (9.1 mg, 0.03 mmol), **2b** (43.2 mg, 0.6 mmol), and 1,1,1,2-tetrachloroethane (ca. 15 mg) as an internal standard in deuterated benzene (1 mL) was irradiated in a NMR tube with a Pyrex filtered light (>300 nm) at room temperature under an argon atmosphere. After the almost quantitative conversion of **1**, the product distributions were determined by ^{1}H NMR, occasionally with removal of the unconsumed alkene. For the preparative runs, a mixture of **1** (90.6 mg, 0.3 mmol) and **2b** (432 mg, 6 mmol) in deaerated benzene (10 mL) was irradiated in a Pyrex tube at room temperature under argon atmosphere. These reactions necessitated a 3-fold longer irradiation time than in an NMR tube. After removal of the solvent and the unconsumed **2b** under reduced pressure, the reaction mixture was column chromatographed on silica gel to give the major product *endo*-**3b** with a mixture of hexane and benzene as an eluent. The minor *endo*-**3b**, *endo*- and *exo*-**4b** were separated by HPLC equipped with a semifractionation column. The analytical data for *endo*-**3b** were described elsewhere.[14] The structures of *endo*-**3a**, *endo*-**3c**−**g**, *exo*-**3a**−**h**, *endo*-**4a**−**g**, *exo*-**4a**−**g**, **6a**−**e**, and **7d**,**e** were confirmed by ^{1}H and ^{13}C NMR, IR, mass spectra, as well as the elemental analyses (for each major isomer). From the Karplus equation, the coupling constant between the adjacent *cis*-methines in cyclobutane ring can be estimated to be larger than that for the *trans*-methines. This was substantially applicable to other cyclobutane products *endo*- and *exo*-**3**, **4**.

(1*R,3*S**,5*S**,7*R**,9*S**)-1,5-Dimethyl-9-phenoxy-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-3a).** ^{1}H NMR ($CDCl_3$): δ 0.83 (s, 3H), 1.63 (s, 3H), 1.93 (ddd, 1H, J = 10.2, 2.6, 2.6 Hz), 2.18 (ddd, 1H, J = 13.2, 2.6, 1.0 Hz), 2.70 (ddd, 1H, J = 13.2, 10.2, 4.9 Hz), 3.13 (s, 1H), 4.36 (ddd, 1H, J = 4.9, 2.6, 1.0 Hz), 6.64 (d, 2H, J = 7.3 Hz), 6.93 (t, 1H, J = 7.3 Hz), 7.16−7.44 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 18.7, 19.9, 32.2, 43.3, 48.4, 49.8, 50.1, 52.1, 81.8, 115.0, 121.4, 127.2, 127.9, 128.3, 128.8, 128.9, 129.4, 129.7, 139.1, 141.0, 155.9, 205.9, 209.5. Anal. Calcd for $C_{29}H_{26}O_3$: C, 82.44; H, 6.20. Found: C, 82.24; H, 6.32.

(1*R,3*S**,5*S**,7*R**,9*R**)-1,5-Dimethyl-9-phenoxy-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-3a).** ^{1}H NMR ($CDCl_3$): δ 0.80 (s, 3H), 1.25 (s, 3H), 1.80 (ddd, 1H, J = 11.2, 2.6, 1.3 Hz), 2.48 (ddd, 1H, J = 12.2, 11.2, 8.9 Hz), 2.65 (ddd, 1H, J = 12.2, 7.6, 2.6 Hz), 3.06 (s, 1H), 4.55 (ddd, 1H, J = 8.9, 7.6, 1.3 Hz), 6.80 (d, 2H, J = 7.3 Hz), 6.95 (t, 1H, J = 7.3 Hz), 7.17−7.34 (m, 10H), 7.40 (d, 2H, J = 7.3 Hz).

(1*S,3*S**,5*S**,7*S**,8*R**)-1,5-Dimethyl-8-phenoxy-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-4a).** The product *endo*-**4a** could not be separated from a mixture with *endo*-**3a** (*endo*-**3a**:*endo*-**4a** = 3:1). The selected data for ^{1}H NMR ($CDCl_3$): δ 0.63 (s, 3H), 1.23 (s, 3H), 2.38−2.52 (m, 2H), 2.64 (dd, 1H, J = 8.6, 2.3 Hz), 3.00 (s, 1H), 4.78 (ddd, 1H, J = 8.6, 6.6, 6.6 Hz), 6.77 (d, 2H, J = 7.6 Hz).

(1*S,3*S**,5*S**,7*S**,8*S**)-1,5-Dimethyl-8-phenoxy-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-4a).** ^{1}H NMR ($CDCl_3$): δ 0.72 (s, 3H), 1.23 (s, 3H), 2.12 (ddd, 1H, J = 13.5, 3.6, 2.6 Hz), 2.37 (ddd, 1H, J = 3.6, 2.3, 1.0 Hz), 2.71 (ddd, 1H, J = 13.5, 7.3, 1.0 Hz), 3.05 (s, 1H), 4.62 (ddd, 1H, J = 7.3, 2.6, 2.3 Hz), 6.99 (d, 2H, J = 7.6 Hz), 7.16−7.39 (m, 13H).

(1*R,3*S**,5*S**,7*R**,9*R**)-9-Ethoxy-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-3b).** ^{1}H NMR ($CDCl_3$): δ 0.69 (s, 3H), 1.13 (t, 3H, J = 6.9 Hz), 1.18 (s, 3H), 1.58 (ddd, 1H, J = 11.2, 2.3, 1.6 Hz), 2.26 (ddd, 1H, J = 11.9, 11.2, 9.6 Hz), 2.42 (ddd, 1H, J = 11.9, 7.9, 2.3 Hz), 3.00 (s, 1H), 3.28 (dq, 1H, J = 9.3, 6.9 Hz), 3.62 (dq, 1H, J = 9.3, 6.9 Hz), 3.88 (ddd, 1H, J = 9.6, 7.9, 1.6), 7.16−7.41 (m, 10H).

(1*S,3*S**,5*S**,7*S**,8*R**)-8-Ethoxy-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-4b).** ^{1}H NMR ($CDCl_3$): δ 0.61 (s, 3H), 1.16 (t, 3H, J = 6.9 Hz), 1.20 (s, 3H), 2.25 (ddd, 1H, J = 12.5, 7.6, 2.0 Hz), 2.27 (dd, 1H, J = 12.5, 7.6 Hz), 2.37 (dd, 1H, J = 8.6, 2.0 Hz), 2.93 (s, 1H), 3.35 (dq, 1H, J = 9.3, 6.9 Hz), 3.64 (dq, 1H, J = 9.3, 6.9 Hz), 4.07 (ddd, 1H, J = 8.6, 7.6, 7.6), 7.16−7.41 (m, 10H).

(1*S,3*S**,5*S**,7*S**,8*S**)-8-Ethoxy-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-4b).** ^{1}H NMR ($CDCl_3$): δ 0.45 (s, 3H), 1.17 (t, 3H, J = 6.9 Hz), 1.18 (s, 3H), 1.96 (ddd, 1H, J = 12.9, 5.3, 2.0 Hz), 2.39 (ddd, 1H, J = 4.0, 2.0, 1.6 Hz), 2.56 (ddd, 1H, J = 12.9, 7.9, 1.6 Hz), 2.97 (s, 1H), 3.34 (dq, 1H, J = 9.2, 6.9 Hz), 3.59 (dq, 1H, J = 9.2, 6.9 Hz), 3.94 (ddd, 1H, J = 7.9, 5.3, 4.0), 7.16−7.39 (m, 10H).

(1*S,3*S**,5*S**,7*R**,9*S**)-9-Cyano-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-3c).** ^{1}H NMR (CD_3OD): δ 0.78 (s, 3H), 1.17 (s, 3H), 2.02 (ddd, 1H, J = 10.2, 3.0, 2.0 Hz), 2.26 (ddd, 1H, J = 12.2, 3.0, 3.0 Hz), 2.84 (ddd, 1H, J = 12.2, 10.2, 8.9 Hz), 2.97 (ddd, 1H, J = 8.9, 3.0, 2.0 Hz), 3.17 (s, 1H), 7.18−7.44 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 18.6, 21.6, 28.3, 33.4, 44.5, 48.8, 49.3, 50.7, 50.9, 118.8, 127.4, 128.1, 128.9, 129.0, 129.6, 138.5, 140.4, 204.6, 208.3. IR (KBr): 1684 cm^{-1}. MS (EI): *m*/*e* 355 (M^+). Anal. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.95; N, 3.94. Found: C, 80.80; H, 6.05; N, 3.85.

(1*S,3*S**,5*S**,7*R**,9*R**)-9-Cyano-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-3c).** ^{1}H NMR ($CDCl_3$): δ 0.86 (s, 3H), 1.21 (s, 3H), 1.94 (ddd, 1H, J = 10.2, 3.0, 1.3 Hz), 2.49 (ddd, 1H, J = 12.2, 9.2, 3.0 Hz), 2.54 (ddd, 1H, J = 12.2, 10.2, 10.2 Hz), 3.05 (s, 1H), 3.14 (ddd, 1H, J = 10.2, 9.2, 1.3 Hz), 7.17−7.40 (m, 10H). The selected data of **5c** and **6c** for ^{1}H NMR (C_6D_6) are either δ 0.32 (s, 3H) or δ 0.70 (s, 3H).

(1*R,3*S**,5*S**,7*R**,9*S**)-9-Acetoxy-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-3d).** ^{1}H NMR (C_6D_6): δ 0.54 (s, 3H), 1.19 (s, 3H), 1.62 (s, 3H), 1.89 (ddd, 1H, J = 9.6, 4.6, 2.3 Hz), 2.13 (ddd, 1H, J = 13.2, 4.6, 3.6 Hz), 2.28 (ddd, 1H, J = 13.2, 9.6, 5.9 Hz), 2.98 (s, 1H), 4.65 (ddd, 1H, J = 5.9, 3.6, 2.3 Hz), 6.73−7.30 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 19.0, 20.4, 21.0, 32.5, 42.8, 47.8, 48.9, 49.9, 52.6, 77.8, 127.2, 128.0, 128.2, 128.8, 129.0, 129.8, 138.7, 140.8, 169.2, 205.3, 209.0. IR (KBr): 1684, 1748 cm^{-1}. MS (EI): *m*/*e* 388 (M^+). Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.24; H, 6.39.

(1*R,3*S**,5*S**,7*R**,9*R**)-9-Acetoxy-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-3d).** ^{1}H NMR ($CDCl_3$): δ 0.72 (s, 3H), 1.21 (s, 3H), 1.72 (ddd, 1H, J = 11.2, 2.3, 1.3 Hz), 2.02 (s, 3H), 2.36 (ddd, 1H, J = 11.9, 11.2, 9.5 Hz), 2.54 (ddd, 1H, J = 11.9, 7.9, 2.3 Hz), 3.04 (s, 1H), 5.10 (ddd, 1H, J = 9.5, 7.9, 1.3 Hz), 7.16−7.41 (m, 10H).

(1*S,3*S**,5*S**,7*S**,8*R**)-8-Acetoxy-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-4d) and (1*S**,3*S**,5*S**,7*S**,8*S**)-8-Acetoxy-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-**

dione (*exo*-4d). These products could not be isolated from each other. However, the stereochemistry was deduced by comparison of the coupling constant of the most downfield methine proton (adjacent to acetoxy group) with those of *endo*-**4b** and *exo*-**4b** which also allowed the determination of respective yields. The ^{1}H NMR (C_6D_6) data for *endo*-**4d**, δ 5.17 (ddd, 1H, J = 8.9, 8.9, 7.6 Hz); *exo*-**4d**, δ 3.89 (ddd, 1H, J = 5.9, 5.9, 4.0 Hz).

(1*S,3*S**,5*S**,7*R**,9*R**)-9-(4-Methoxyphenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-3e).** ^{1}H NMR ($CDCl_3$): δ 0.83 (s, 3H), 1.02 (s, 3H), 2.05 (ddd, 1H, J = 10.9, 3.6, 1.7 Hz), 2.34 (s, 1H), 2.54 (ddd, 1H, J = 12.9, 4.3, 3.6 Hz), 2.82 (ddd, 1H, J = 12.9, 10.9, 9.2 Hz), 3.21 (ddd, 1H, J = 9.2, 4.3, 1.7 Hz), 3.76 (s, 3H), 6.83 (d, 2H, J = 8.6 Hz), 7.1 (d, 2H, J = 8.6 Hz), 7.16−7.41 (m, 10H).

(1*S,3*S**,5*S**,7*R**,9*S**)-9-(4-Methoxyphenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-3e).** ^{1}H NMR ($CDCl_3$): δ 0.36 (s, 3H), 1.28 (s, 3H), 1.70 (dd, 1H, J = 10.6, 2.0 Hz), 2.35 (ddd, 1H, J = 11.5, 8.6, 2.0 Hz), 2.61 (ddd, 1H, J = 11.5, 11.5, 10.6 Hz), 3.08 (s, 1H), 3.63 (dd, 1H, J = 11.5, 8.6 Hz), 3.77 (s, 3H), 6.82 (d, 2H, J = 8.6 Hz), 7.1 (d, 2H, J = 8.6 Hz), 7.16−7.44 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 16.1, 18.4, 29.4, 43.5, 44.6, 47.1, 47.9, 49.8, 52.4, 55.2, 113.6, 126,4, 127.2, 127.9, 128.3, 128.4, 128.8, 128.9, 129.8, 138.6, 141.0, 158.5, 206.9, 211.0. IR (KBr): 1680 cm^{-1}. Anal. Calcd for $C_{30}H_{28}O_3$: C, 82.54; H, 6.46. Found: C, 82.46; H, 6.53.

(1*S,3*S**,5*S**,7*R**,8*R**)-8-(4-Methoxyphenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-4e).** ^{1}H NMR ($CDCl_3$): δ 0.71 (s, 3H), 0.87 (s, 3H), 2.20 (ddd, 1H, J = 12.2, 9.2, 2.3 Hz), 2.50 (ddd, 1H, J = 10.9, 2.3, 1.0 Hz), 2.70 (ddd, 1H, J = 12.2, 10.2, 1.0 Hz), 2.96 (s, 1H), 3.78 (s, 3H), 3.85 (ddd, 1H, J = 10.9, 10.2, 9.2 Hz), 6.82−6.87 (m, 2H), 7.02−7.06 (m, 2H), 7.12−7.36 (m, 10H).

(1*S,3*S**,5*S**,7*R**,8*S**)-8-(4-Methoxyphenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-4e).** ^{1}H NMR (C_6D_6): δ 0.33 (s, 3H), 1.18 (s, 3H), 1.99 (dd, 1H, J = 11.9, 9.6 Hz), 2.58 (ddd, 1H, J = 11.9, 9.6, 1.0 Hz), 2.78 (dd, 1H, J = 8.2, 1.0 Hz), 2.94 (s, 1H), 3.31 (s, 3H), 3.47 (ddd, 1H, J = 9.6, 9.6, 8.2 Hz), 6.70−7.45 (m, 14H).

(1*S,3*S**,5*S**,7*R**,9*R**)-9-(4-Chlorophenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-3f).** ^{1}H NMR ($CDCl_3$): δ 0.84 (s, 3H), 1.02 (s, 3H), 2.09 (ddd, 1H, J = 10.6, 3.3, 1.6 Hz), 2.36 (s, 1H), 2.53 (ddd, 1H, J = 13.2, 4.3, 3.3 Hz), 2.70 (ddd, 1H, J = 13.2, 10.6, 9.2 Hz), 3.23 (ddd, 1H, J = 9.2, 4.3, 1.6 Hz), 7.03 (d, 2H, J = 8.2 Hz), 7.11−7.30 (m, 12H).

(1*S,3*S**,5*S**,7*R**,9*S**)-9-(4-Chlorophenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-3f).** ^{1}H NMR ($CDCl_3$): δ 0.35 (s, 3H), 1.28 (s, 3H), 1.72 (dd, 1H, J = 9.6, 1.6 Hz), 2.39 (ddd, 1H, J = 11.5, 8.6, 1.6 Hz), 2.59 (ddd, 1H, J = 11.5, 11.5, 9.6 Hz), 3.09 (s, 1H), 3.63 (dd, 1H, J = 11.5, 8.6 Hz), 6.01 (d, 2H, J = 8.2 Hz), 7.14−7.44 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 16.2, 18.4, 29.1, 43.6, 44.3, 47.2, 47.8, 50.0, 52.1, 127,3, 128.0, 128.2, 128.6, 128.8, 128.9, 129.7, 132.6, 136.2, 138.3, 140.8, 206.9, 210.7. IR (KBr): 1680 cm^{-1}. Anal. Calcd for $C_{29}H_{25}ClO_2$: C, 78.99; H, 5.71. Found: C, 78.96; H, 5.81.

(1*S,3*S**,5*S**,7*R**,8*R**)-8-(4-Chlorophenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-4f).** ^{1}H NMR ($CDCl_3$): δ 0.74 (s, 3H), 0.89 (s, 3H), 2.20 (ddd, 1H, J = 11.9, 8.6, 2.3 Hz), 2.49 (ddd, 1H, J = 10.6, 2.3, 1.0 Hz), 2.70 (dd, 1H, J = 11.9, 10.6, 1.0 Hz), 2.97 (s, 1H), 3.86 (ddd, 1H, J = 10.6, 10.6, 8.6 Hz), 7.04 (d, 2H, J = 8.2 Hz), 7.14−7.36 (m, 12H).

(1*S,3*S**,5*S**,7*R**,8*S**)-8-(4-Chlorophenyl)-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-4f).** ^{1}H NMR ($CDCl_3$): δ 0.25 (s, 3H), 1.24 (s, 3H), 2.20 (dd, 1H, J = 12.2, 9.2 Hz), 2.65 (dd, 1H, J = 7.9, 1.0 Hz), 2.72 (ddd, 1H, J = 12.2, 9.6, 1.0 Hz), 3.08 (s, 1H), 3.86 (ddd, 1H, J = 9.6, 9.2, 7.9), 7.03 (d, 2H, J = 8.2 Hz), 7.13−7.42 (m, 12H).

(1*R,3*S**,5*S**,7*R**,9*S**)-9-Carbazol-9-yl-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-3g).** ^{1}H NMR ($CDCl_3$): δ 0.53 (s, 3H), 1.39 (s, 3H), 2.73 (dd, 1H, J = 10.6, 7.6 Hz), 2.92 (s, 1H), 3.09 (ddd, 1H, J = 13.8, 10.6, 10.2 Hz), 3.69 (ddd, 1H, J = 13.8, 9.2, 7.6 Hz), 4.97 (dd, 1H, J = 10.2, 9.2 Hz), 7.14−7.64 (m, 16H), 8.07 (d, 2H, J = 7.6 Hz).

(1*R,3*S**,5*S**,7*R**,9*R**)-9-Carbazol-9-yl-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.03,5]nonane-2,6-dione (*exo*-3g).** ^{1}H NMR ($CDCl_3$): δ 0.61 (s, 3H), 1.37 (s, 3H), 2.30 (ddd, 1H, J = 11.2, 4.0, 1.0 Hz), 2.80 (ddd, 1H, J = 12.5, 9.9, 4.0 Hz), 3.27 (s, 1H), 3.90 (ddd, 1H, J = 12.5, 11.2, 9.9 Hz), 5.30 (ddd, 1H, J = 9.9, 9.9, 1.0 Hz), 7.16−7.46 (m, 16H), 8.01 (d, 2H, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 16.6, 18.8, 31.2, 43.4, 46.9, 47.0, 49.8, 55.7, 57.3, 110.5, 119.7, 120.4, 123.6, 125.7, 127.4, 128.0, 128.3, 128.9, 129.0, 129.8, 138.3, 140.6, 140.8, 206.4, 209.6. IR (KBr): 1682 cm^{-1}. Anal. Calcd for $C_{35}H_{29}NO_2$: C, 84.82; H, 5.90; N, 2.83. Found: C, 84.88; H, 6.08; N, 3.00.

(1*S,3*S**,5*S**,7*S**,8*R**)-8-Carbazol-9-yl-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*endo*-4g).** ^{1}H NMR ($CDCl_3$): δ 0.83 (s, 3H), 0.89 (s, 3H), 2.53 (ddd, 1H, J = 12.5, 9.6, 2.6 Hz), 2.73 (ddd, 1H, J = 10.5, 2.6, 1.0 Hz), 3.26 (s, 1H), 3.88 (ddd, 1H, J = 12.5, 11.2, 0.7 Hz), 5.30 (dd, 1H, J = 11.2, 10.5, 9.6 Hz), 7.13−7.41 (m, 16H), 8.08 (d, 2H, J = 7.6 Hz).

(1*S,3*S**,5*S**,7*S**,8*S**)-8-Carbazol-9-yl-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-4g).** ^{1}H NMR ($CDCl_3$): δ 0.48 (s, 3H), 1.31 (s, 3H), 2.82 (ddd, 1H, J = 12.5, 9.6, 1.0 Hz), 3.21 (dd, 1H, J = 12.5, 10.6 Hz), 3.21 (s, 1H), 3.87 (dd, 1H, J = 9.2, 0.7 Hz), 5.32 (dd, 1H, J = 10.5, 9.6 Hz), 7.16−7.45 (m, 16H), 8.07 (d, 2H, J = 7.6 Hz).

(1*S,3*S**,5*S**,7*R**,9*R**)-9-*tert*-Butyl-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]nonane-2,6-dione (*exo*-3h).** mp 184−186 °C, colorless prisms. ^{1}H NMR (C_6D_6): δ 0.76 (s, 3H), 0.79 (s, 9H), 1.19 (s, 3H), 1.61 (dd, 1H, J = 9.2, 1.6 Hz), 2.01 (ddd, 1H, J = 11.2, 9.6, 9.2 Hz), 2.16 (ddd, 1H, J = 9.6, 7.9, 1.6 Hz), 2.23 (dd, 1H, J = 11.2, 7.9 Hz), 2.89 (s, 1H), 6.76−6.96 (m, 6H), 7.21−7.33 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 16.1, 18.3, 27.9, 28.7, 33.8, 42.6, 46.1, 48.5, 49.1, 50.8, 53.7, 127.2, 127.7, 128.3, 128.7, 128.8, 129.8, 138.5, 141.0, 206.3, 212.0. Anal. Calcd for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.60; H, 8.04.

(1*R,3*S**,5*S**,7*R**)-8,9-Diethyl-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]non-8-ene-2,6-dione (6a).** mp 147−149 °C, colorless prisms. ^{1}H NMR ($CDCl_3$): δ 0.41 (s, 3H), 1.00 (t, 6H, J = 7.6 Hz), 1.11 (s, 3H), 1.88−2.17 (m, 4H), 2.58 (br, 1H), 2.81 (s, 1H), 7.17−7.48 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 12.2, 12.5, 18.0, 18.3, 19.2, 20.2, 38.9, 43.2, 47.4, 55.8, 59.1, 127.1, 127.5, 128.0, 128.5, 128.7, 130.3, 138.4, 140.9, 141.8, 148.3, 206.1, 207.1. IR (KBr): 1675 cm^{-1}. Anal. Calcd for $C_{27}H_{28}O_2$: C, 84.34; H, 7.34. Found: C, 84.20; H, 7.46.

(1*R,3*S**,5*S**,7*R**)-8,9-Dimethyl-4,4,8,9-tetraphenyltricyclo[5.2.0.0^{3,5}]non-8-ene-2,6-dione (6b).** mp 159−161 °C, colorless prisms. ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 3H), 1.04 (s, 3H), 2.97 (s, 1H), 3.23 (s, 1H), 7.16−7.56 (m, 20H). ^{13}C NMR ($CDCl_3$): δ 18.2, 18.4, 39.0, 42.7, 46.5, 56.7, 59.7, 123.6, 125.4, 125.5, 125.9, 127.0, 127.1, 127.3, 127.6, 127.7, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8, 130.7, 132.4, 132.5, 138.3, 138.9, 140.7, 143.9, 150.9, 205.7, 205.8. IR (KBr): 1682 cm^{-1}. Anal. Calcd for $C_{35}H_{28}O_2$: C, 87.47; H, 5.87. Found: C, 87.28; H, 6.11.

(1*R,3*S**,5*S**,7*R**)-9-Butyl-1,5-dimethyl-4,4-diphenyltricyclo[5.2.0.0^{3,5}]non-8-ene-2,6-dione (6c).** mp 116−118 °C, colorless prisms. ^{1}H NMR ($CDCl_3$): δ 0.43 (s, 3H), 0.87 (t, 3H, J = 6.9 Hz), 1.13 (s, 3H), 1.23−1.41 (m, 4H), 1.87−1.93 (m, 2H), 2.64 (td, 1H, J = 2.6, 1.6 Hz), 2.86 (s, 1H), 5.68 (dt, 1H, J = 1.6, 1.6 Hz), 7.14−7.39 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 13.9, 17.7, 18.2, 22.5, 26.3, 27.5, 39.5, 44.1, 47.6, 57.7, 58.5, 126.5, 127.1, 127.7, 128.4, 128.7, 128.9, 130.4, 138.4, 140.8, 157.5, 205.6, 208.0. IR (KBr): 1682 cm^{-1}. Anal. Calcd for $C_{27}H_{28}O_2$: C, 84.34; H, 7.34. Found: C, 84.37; H, 7.64.

(1*R,3*S**,5*S**,7*R**)-1,5-Dimethyl-4,4,9-triphenyltricyclo[5.2.0.0^{3,5}]-non-8-ene-2,6-dione (6d).** ^{1}H NMR ($CDCl_3$): δ 0.72 (s, 3H), 1.13 (s,

3H), 2.79 (dt, 1H, J = 2.0 Hz), 2.93 (s, 1H), 6.29 (d, 1H, J = 2.0 Hz), 7.16−7.42 (m, 13H), 7.58 (dd, 2H, J = 8.2, 1.6 Hz). ^{13}C NMR ($CDCl_3$): δ 18.0, 19.0, 39.4, 44.2, 47.4, 58.2, 58.3, 125.7, 126.3, 127.2, 127.8, 128.3, 128.4, 128.7, 128.8, 128.9, 130.3, 131.1, 138.2, 140.7, 151.3, 205.7, 207.2. Anal. Calcd for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 86.24; H, 6.23.

(1*S,3*S**,5*S**,7*R**)-1,5-Dimethyl-4,4,8-triphenyltricyclo[5.2.0.0^{3,5}]-non-8-ene-2,6-dione (7d).** ^{1}H NMR ($CDCl_3$): δ 0.53 (s, 3H), 1.05 (s, 3H), 2.90 (s, 1H), 3.23 (s, 1H), 6.32 (s, 1H), 7.16−7.42 (m, 13H), 7.58 (d, 2H, J = 8.2 Hz).

(1*R,3*S**,5*S**,7*R**)-1,5,8-Trimethyl-4,4,9-triphenyltricyclo[5.2.0.0^{3,5}]-non-8-ene-2,6-dione (6e).** mp 175−177 °C, colorless prisms. ^{1}H NMR ($CDCl_3$): δ 0.67 (s, 3H), 1.11 (s, 3H), 2.01 (d, 3H, J = 1.6 Hz), 2.62 (q, 1H, J = 1.6 Hz), 2.87 (s, 1H), 7.15−7.42 (m, 13H), 7.56 (d, 2H, J = 8.2 Hz). ^{13}C NMR ($CDCl_3$): δ 14.0, 18.0, 18.8, 38.9, 43.2, 47.2, 56.2, 61.5, 126.7, 127.2, 127.7, 128.3, 128.5, 128.7, 128.8, 130.5, 132.6, 138.0, 138.2, 140.8, 143.4, 206.0, 206.1. IR (KBr): 1679 cm^{-1}. Anal. Calcd for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26. Found: C, 86.09; H, 6.47.

(1*R,3*S**,5*S**,7*R**)-1,5,9-Trimethyl-4,4,8-triphenyltricyclo[5.2.0.0^{3,5}]-non-8-ene-2,6-dione (7e).** ^{1}H NMR ($CDCl_3$): δ 0.46 (s, 3H), 1.02 (s, 3H), 1.90 (d, 3H, J = 2.3 Hz), 2.85 (s, 1H), 3.14 (q, 1H, J = 2.3 Hz), 7.15−7.42 (m, 13H), 7.52 (d, 2H, J = 8.2 Hz).

Trapping Experiment of 1,4-Biradical in the Photoreaction of 1 with 2b by Benzeneselenol. A mixture of **1** (90.6 mg, 0.30 mmol), **2b** (432 mg, 6 mmol), and benzeneselenol (236 mg, 1.5 mmol) in deaerated benzene (10 mL) was irradiated by a 300 W mercury light (>300 nm) under argon atmosphere at room temperature for 3 h. After removal of the solvent and excess **2b** under reduced pressure, the residue was submitted for ^{1}H NMR analysis to determine the product yields by using 1,1,1,2-tetrachloroethane as an internal standard. The reaction mixture was found to contain the radical trapped **8** (34%) and **9** (9%) along with *endo*-**3b** (15%), *exo*-**3b** (3%), *endo*-**4b** (4%), *exo*-**4b** (2%), and **10** (6%). After the preliminary column chromatographic separation of a mixture of **8** and **9** on silica gel with dichloromethane as an eluent, the major product **8** was isolated by preparative HPLC and purified by recrystallization from benzene/hexane. However, the minor isomer **9** was obtained only with contamination of **8**. The structures of **8** and **9** were determined as follows.

(1*S,3*R**,4*R**,6*S**)-3-(2-Ethoxyethyl)-1,4-dimethyl-7,7-diphenylbicyclo[4.1.0]heptane-2,5-dione (8).** mp 138−139 °C, colorless needles. ^{1}H NMR ($CDCl_3$): δ 0.90 (d, 3H, J = 6.6 Hz), 1.11 (t, 3H, J = 6.9 Hz), 1.14−1.25 (m, 1H), 1.20 (s, 3H), 1.63−1.80 (m, 2H), 2.38 (dq, 1H, J = 13.2, 6.6 Hz), 2.91 (s, 1H), 3.12 (dq, 1H, J = 9.2, 6.9 Hz), 3.26−3.46 (m, 3H), 7.15−7.47 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 13.6, 15.3, 18.4, 27.4, 36.7, 46.9, 47.6, 47.8, 49.3, 66.0, 68.4, 127.1, 127.6, 128.4, 128.8, 129.1, 129.2, 140.0, 141.3, 206.7, 207.3. IR (KBr): 1687 cm^{-1}. MS (EI): *m*/*e* 376 (M^+). Anal. Calcd for $C_{25}H_{28}O_3$: C, 79.75; H, 7.50. Found: C, 79.65; H, 7.61.

(1*S,4*S**,6*S**)-4-(2-Ethoxyethyl)-1,4-dimethyl-7,7-diphenylbicyclo-[4.1.0]heptane-2,5-dione (9).** A mixture with **8** (**8**:**9** = 3:1). Selected ^{1}H NMR ($CDCl_3$): δ 0.76 (s, 3H), 1.14 (t, 3H, J = 6.9 Hz), 1.22 (s, 3H), 1.27 (d, 1H, J = 17.1 Hz), 2.17 (d, 1H, J = 17.1 Hz). MS (EI): *m*/*e* 376 (M^+).

Photoreaction of 1 with Benzeneselenol. A mixture of **1** (90.6 mg, 0.30 mmol) and benzeneselenol (236 mg, 1.5 mmol) in deaerated benzene (10 mL) was irradiated as above. After removal of the solvent under reduced pressure, the residue was submitted for ^{1}H NMR analysis to determine the conversion (20%) of **1** and the yield of sole product **10** (~100% based on consumed **1**) by using 1,1,1,2-tetrachloroethane as an internal standard. The compound **10** was isolated on silica gel column chromatography with dichloromethane/hexane as an eluent and was identified as reported previously.[23b]

Trapping Experiment of Cation Radical in the Photoreaction of 1 and Chloranil with 2g by Methanol. A mixture of **1** (9.1 mg, 0.03 mmol) and **2g** (29.0 mg, 0.15 mmol) in benzene (1 mL) in the presence of methanol (96 mg, 3 mmol) was irradiated by a 300 W light in a NMR tube through a Pyrex filter under argon atmosphere at room temperature for 5 h. After the removal of methanol by evaporation, the reaction residue was submitted for NMR analysis to show the formation of usual [2 + 2] adducts but no indication of methanol adduct. However, a similar photoreaction of chloranil with **2g** under the same reaction conditions gave the methanol adduct **11** quantitatively, which was isolated by silica gel chromatography with benzene/hexane as an eluent and was identified as previously reported.[39] The ^{1}H NMR spectrum is as follows: δ 1.46 (d, 3H, J = 5.9 Hz), 2.81 (s, 3H), 5.40 (q, 1H, J = 5.9 Hz), 7.21 (t, 2H, J = 7.9 Hz), 7.36 (t, 2H, J = 7.9 Hz), 7.48 (d, 2H, J = 7.9 Hz), 8.02 (d, 2H, J = 7.9 Hz).

X-ray Crystal and Molecular Structure Analyses. The X-ray data were measured on Mac Science MXC3 (for **1** and *exo*-**3e**) and Rigaku RAXIS-RAPID Imaging plate (for *exo*-**3h**) using graphite-monochromated Mo Kα radiation at room temperature. The structures were solved by SIR92 and refined by full-matrix least-squares. All hydrogen atoms of **1**, *exo*-**3e**, and *exo*-**3h** except for H12, H13, H15, H16, H31A, H31B, and H31C of *exo*-**3e** were found in the difference Fourier map. All non-hydrogen atoms were refined with anisotropic displacement parameters, and all hydrogen atoms were isotropically refined. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 173916 (**1**), CCDC 173917 (*exo*-**3e**), and CCDC 173918 (*exo*-**3h**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving-.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Crystal Data for 1. $C_{21}H_{18}O_2$, M = 302.37, monoclinic, space group $P2_1/a$, a = 12.32(1), b = 16.69(1), c = 8.076(3) Å, β = 94.64(5)°, V = 1655(2) Å^3, Z = 4, D_c = 1.214 g/cm^3, R = 0.054 and R_w = 0.057 for 2609 reflections with $I > 2.0\sigma(I)$.

Crystal Data for *exo*-3e. $C_{30}H_{28}O_3$, M = 436.55, monoclinic, space group $P2_1/c$, a = 21.495(9), b = 12.480(7), c = 8.88(1) Å, β = 92.50(6), V = 2379(3) Å^3, Z = 4, D_c = 1.219 g/cm^3, R = 0.088 and R_w = 0.103 for 2080 reflections with $I > 2.0\sigma(I)$.

Crystal Data for *exo*-3h. $C_{27}H_{30}O_2$, M = 386.53, monoclinic, space group $P2_1/n$, a = 10.8087(5), b = 27.450(2), c = 14.9497(9) Å, β = 99.183(2), V = 4378.7(4) Å^3, Z = 8, D_c = 1.173 g/cm^3, R = 0.056 and $R_w = [(\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)]^{1/2}$ = 0.152 for 9293 reflections with $I > 2.0\sigma(I)$.

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Supporting Information Available: X-ray structural data for **1**, *exo*-**3e**, and *exo*-**3h**, and summary table of ^{1}H NMR data (270 MHz) for compounds *endo*- and *exo*-**3**, **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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