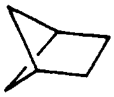
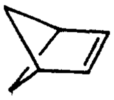
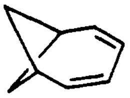
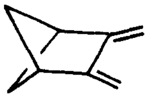
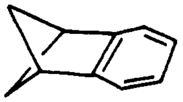
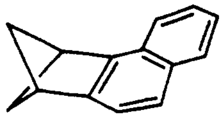
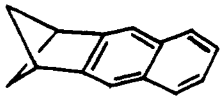
For the Hückel calculations all βs between orbitals on the same carbon were taken to be zero and the βs between orbitals on adjacent carbons were taken to be ±0.5 with the sign determined by whether the overlap was between lobes of the same sign ($\beta = -0.5$) or of opposite sign ($\beta = +0.5$). The βs for the p_z orbitals on the unsaturated moiety were taken to be −1.0 in the usual Hückel fasion as were the βs between the points of attachment of the unsaturated moiety to orbitals 2 and 6 on carbon atoms 1 and 2. The βs for interaction with orbitals 1 and 5 were taken to be zero by reason of symmetry.

The electron density calculated for cyclobutane by this model is unity for all orbitals. With hydrocarbon **3** the calculated population of orbital 3 grows at the expense of orbital 4. The other orbital populations stay the same. With hydrocarbon **7** it is orbital 4 that grows at the expense of orbital 3. With hydrocarbon **11** there is only a small change in the densities of orbitals 3 and 4. These results qualitatively parallel the conclusions drawn from the full INDO calculations and their perturbation analysis. The quantitative relationship between the observed shift increments and the calculated difference in orbital 3 and orbital 4 populations, while less than perfect, are hopefully good enough to identify hydrocarbons with potentially interesting shifts. The equation and a few of the predictions made with it are shown below.

$$\text{shift increment} = 4.2 + 71.1(\text{population of orbital 3} - \text{population of orbital 4})$$

$$\text{average error} = 3.4\ \text{ppm}$$

	$P_3 - P_4$	shift
	0.000	0.0
	+0.301	+28.7
	-0.229	-8.5
	+0.040	+4.4
	+0.169	+16.2*
	+0.201	+18.5*
	+0.128	+13.3*

* predicted

Conclusions

The anomalous shift increments for these strained bicyclic and tricyclic alkenes arise from variations in the local paramagnetic anisotropy term. The sign and magnitude of the shifts can be analyzed in terms of joint *electrostatic* and *magnetic* perturbations. An empirical correlation between the shift increments and changes in carbon 2s population is noted. A simple Hückel-based model accounts for the observed dependence of the shifts on the structure of the unsaturated bridge.

Acknowledgment. We thank P. Bischof for calculating several of the MINDO/3 geometries. The work was facilitated by an Alexander von Humboldt award to C. F. Wilcox, Jr.

[2 + 4] Photocyclization between Quinones and Allenes via Photoinduced Electron Transfer

Kazuhiro Maruyama* and Hiroshi Imahori

Department of Chemistry, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606, Japan

Received November 15, 1988

Photochemical reactions of halo-1,4-naphthoquinones with 1,1-diphenylallenes afforded spiropyran adducts derived from [2 + 4] cycloaddition between carbonyl group of quinone and allene in good yield. In the photoreactions of 2,3-dichloro-1,4-naphthoquinone with monophenylallenes, [2 + 2] cycloadducts were obtained in addition to spiropyran derivatives. Considering the relationship between formation of spiropyran adducts and the free energy changes (ΔG) together with substituent effects, solvent effects, and CIDNP (chemically induced dynamic nuclear polarization), we propose an electron-transfer mechanism. That is, radical ion pair formation from excited triplet quinone and allene is followed by conversion to a biradical. Subsequent bond formation between the ketyl radical in quinone moiety and ortho positions of the phenyl substituents on the allene skeleton leads to the spiropyran adduct after subsequent 1,5-hydrogen shift.

Since about 20 years ago we have been engaged into the photochemistry of quinones to explore novel photochemical reactions.[1] Specifically, photochemical reactions of halo-1,4-naphthoquinones with 1,1-diphenylethylenes have been extended remarkably.[2] The reactions proceed by substitution of a halogen atom with the ethylenic group (ethylene adduct), and subsequent photocyclizations result

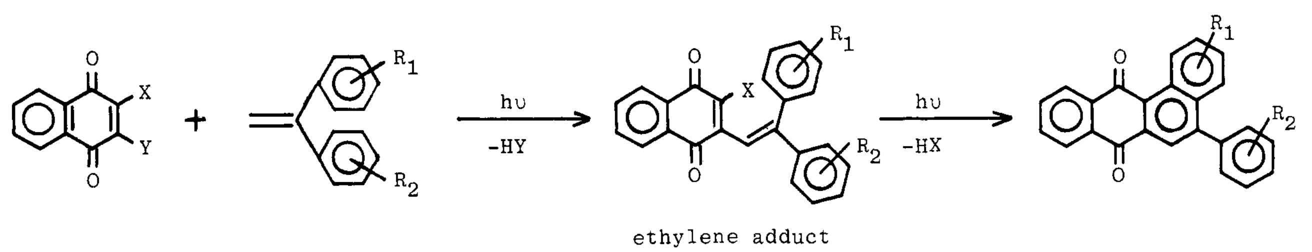
---

[1] (a) Bruce, J. M. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; John Wiley & Sons: New York, 1974; Vol. 1, Part 1, Chapter 9. (b) Maruyama, K.; Osuka, A. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1988; Vol. 2, Part 1, Chapter 13, and references therein.

[2] (a) Maruyama, K.; Otsuki, T. *Chem. Lett.* **1975**, 87. (b) Maruyama, K.; Otsuki, T.; Mitsui, K. *J. Org. Chem.* **1980**, *45*, 1424. (c) Maruyama, K.; Otsuki, T.; Tai, S. *Ibid.* **1985**, *50*, 52.

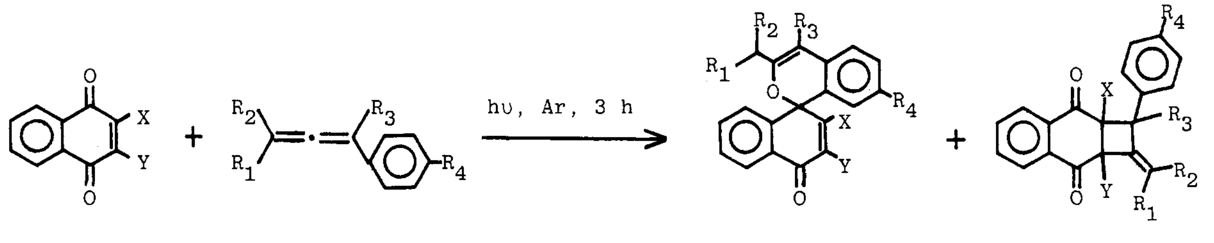
0022-3263/89/1954-2692$01.50/0

Scheme I



X= Cl, Br, OCH_3, H; Y= Cl, Br; R_1, R_2= F, Cl, Br, H, CH_3, OCH_3

Scheme II



1 (0.04 M) 2 (0.08 M) 3 4

in formation of 5-phenylbenz[*a*]anthracene-7,12-diones. It was demonstrated that this reaction proceeds via photoinduced electron transfer, and it extended general synthetic methodoloy of polyaromatic compounds (Scheme I).

The photoexcited chemistry between electron donors and acceptors has found useful application in organic synthesis.[3] A variety of electron donors, 2-alkoxy-1-alkenes[4] and the related silyl enol ethers,[5] allylstannanes,[6] and others,[7] was applicable to the photoinduced electron-transfer reactions of quinones. As a further extension, the reaction of quinones with phenyl-substituted allenes, especially 1,1-diphenylallenes,[8] was examined to give a novel class of polyaromatic compounds.

The photochemistry involving allene cation radicals is one of the current topics from synthetic and mechanistic points of view.[9-15] Johnson reported a photosensitized reaction of the 9,10-dicyanoanthracene or 1,4-dicyanonaphthalene with triphenylallene or tetraphenylallene.[14] Reactions of these allenes in methanol parallel those of 1,1-diphenylethylenes, which were reported by Arnold.[16] Mariano has reported the photoinduced electron-transfer reactions of iminium salts–allene system.[15] In methanol product formations occur via deprotonation or methanol additions to the intermediate allene cation radical followed by coupling of the resulting neutral pair, while in acetonitrile a variety of [2 + 2] and [2 + 4] cycloaddition occurs with a definitive regioselectivity.

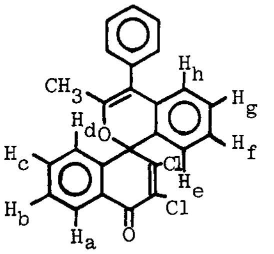


Figure 1. Structure of **3f**.

Photochemical reaction of quinones with allenes have been studied by several groups. For *o*-quinones, Boleij and Bos reported that allenes add photochemically to 9,10-phenanthraquinone to yield dioxin derivatives.[17] For *p*-quinones, Ishibe reported the photoreaction of tetramethylallene with benzoquinone or naphthoquinone to give 5-hydroxyindan-2-one derivatives, which are rearranged products of intermediary oxetane.[18] Ogino reported the photochemical reaction of duroquinone with 1,1-dimethylallene to give [2 + 2] cyclobutane adduct, while none of the product was obtained in the reaction with tetraphenylallene.[19] However, these authors have paid

---

[3] (a) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1983; Vol. 6. (b) Mariano, P. S.; Stavinoha, J. L. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 145. (c) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (d) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 82, and references therein.

[4] Maruyama, K.; Otsuki, T.; Tai, S. *Chem. Lett.* **1984**, 371.

[5] Maruyama, K.; Tai, S.; Imahori, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1777.

[6] Maruyama, K.; Imahori, H.; Osuka, A.; Takuwa, A.; Tagawa, H. *Chem. Lett.* **1986**, 1719. Maruyama, K.; Imahori, H. *Bull. Chem. Soc. Jpn.*, in press. Maruyama, K.; Matano, Y. submitted.

[7] Maruyama, K.; Tamiaki, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1847.

[8] Maruyama, K.; Imahori, H. *Chem. Lett.* **1988**, 725.

[9] Wagner, W.; Levson, K.; Lifshitz, C. *Org. Mass. Spectrosc.* **1980**, *15*, 271. Van Velzen, P. N. T.; Vanderhardt, W. J. *Ibid.* **1981**, *16*, 237.

[10] Takemura, Y.; Shida, T. *J. Chem. Phys.* **1980**, *73*, 4133.

[11] Koppel, H.; Cederbaum, L. S.; Domcke, W.; Shark, S. S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 210 and references therein.

[12] Becker, J. Y.; Zinger, B. *J. Chem. Soc., Perkin Trans. 2* **1982**, 395. Becker, J. Y.; Zinger, B. *Tetrahedron* **1982**, *38*, 1677. Schlagel, G.; Schaffer, H. J. *Chem. Ber.* **1983**, *116*, 960.

[13] Frenking, G.; Schrarz, H. *Int. J. Mass. Spectrom. Ion Phys.* **1983**, *52*, 131. Hasselbach, E. *Chem. Phys. Lett.* **1970**, *7*, 428.

[14] Klett, M. W.; Johnson, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 6615. Klett, M. W.; Johnson, R. P. *Tetrahedron Lett.* **1983**, 1107.

[15] Somekawa, K.; Haddaway, K.; Mariano, P. S.; Tossell, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3060. Haddaway, K.; Somekawa, K.; Fleming, P.; Tossell, J. A.; Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 4239.

[16] (a) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080. (b) Maroulis, A. J.; Shigemitsu, Y.; Arnold, D. R. *Ibid.* **1978**, *100*, 535.

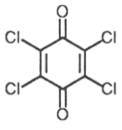
[17] Bos, H. J. T.; Slagt, C.; Boleij, T. S. M. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 1170.

[18] Ishibe, N.; Hashimoto, K.; Yamaguchi, Y. *J. Chem. Soc. Perkin Trans. 1* **1975**, 318.

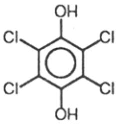
Table I. Photochemical Reactions of Quinones 1 with Allenes 2

run	quinone	allene	solvent	convn of **1**, %	yield of **3**, %^{a}	yield of **4**, %^{a}
1	**1a**: X = Y = Cl	**2a**: $R_1 = R_2 = R_3 = R_4 = H$	PhH	93	**3a**: 0	**4a**: 74
2	**1a**: X = Y = Cl	**2b**: $R_1 = R_2 = R_3 = H$, $R_4 = Me$	PhH	100	**3b**: 8	**4b**: 66
3	**1a**: X = Y = Cl	**2c**: $R_1 = R_2 = R_3 = H$, $R_4 = OMe$	PhH	93	**3c**: 14	**4c**: 0
4	**1a**: X = Y = Cl	**2d**: $R_1 = R_2 = H$, $R_3 = 4\text{-}FC_6H_4$, $R_4 = F$	PhH	47	**3d**: 25	**4d**: 0
5	**1a**: X = Y = Cl	**2e**: $R_1 = R_2 = H$, $R_3 = 4\text{-}ClC_6H_4$, $R_4 = Cl$	PhH	23	**3e**: 61	**4e**: 0
6	**1a**: X = Y = Cl	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	PhH	19	**3f**: 89	**4f**: 0
7	**1a**: X = Y = Cl	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	CH_2Cl_2	18	**3f**: 53	**4f**: 0
8	**1a**: X = Y = Cl	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	MeCN^b	30	**3f**: 33	**4f**: 0
9	**1a**: X = Y = Cl	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	MeOH^c	47	**3f**: 0	**4f**: 0
10	**1a**: X = Y = Cl	**2g**: $R_1 = R_2 = H$, $R_3 = 4\text{-}MeC_6H_4$, $R_4 = Me$	PhH	40	**3g**: 85	**4g**: 0
11	**1a**: X = Y = Cl	**2h**: $R_1 = R_2 = H$, $R_3 = 4\text{-}OMeC_6H_4$, $R_4 = OMe$	PhH	34	**3h**: 0	**4h**: 0
12	**1a**: X = Y = Cl	**2h**: $R_1 = R_2 = H$, $R_3 = 4\text{-}OMeC_6H_4$, $R_4 = OMe$	MeCN^b	47	**3h**: 0	**4h**: 0
13	**1b**: X = Y = Br	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	PhH	46	**3i**: 52	**4i**: 0
14	**1c**: X = H, Y = Cl	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	PhH	64	**3j**: 33	**4j**: 0
15	**1d**: X = Y = H	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	PhH	100	**3k**: 0	**4k**: 0
16	**1e**^{d}	**2f**: $R_1 = R_2 = H$, $R_3 = Ph$, $R_4 = H$	PhH	60	**5**:^{d} 50	
17	**1a**: X = Y = Cl	**2l**: $R_1 = H$, $R_2 = Me$, $R_3 = Ph$, $R_4 = H$	PhH	55	**6**:^{d} 45	
18	**1a**: X = Y = Cl	**2m**: $R_1 = H$, $R_2 = R_3 = Ph$, $R_4 = H$	PhH	0	**3m**: 0	**4m**: 0
19	**1a**: X = Y = Cl	**2n**: $R_1 = R_2 = R_3 = Ph$, $R_4 = H$	PhH	0	**3n**: 0	**4n**: 0

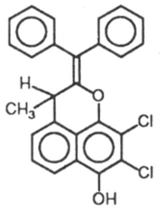
^{a} Isolated yield based on a starting quinone consumed. ^{b} [**1a**] = 0.2 M, [**2f**] = 0.04 M. ^{c} [**1a**] = 0.01 M, [**2f**] = 0.02 M. ^{d}



1e



5



6

no attention to the participation of electron-transfer processes. We report here the photoinduced reactions of quinones with phenyl-substituted allenes via electron-transfer processes.

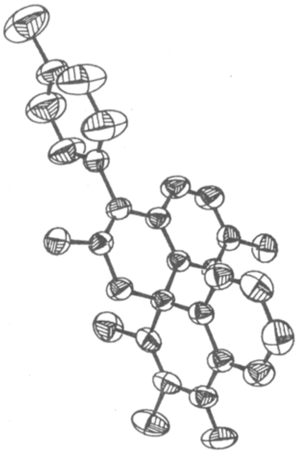


Figure 2. ORTEP view of compound **3g**.

Results

Photochemical Reactions of Quinones with Phenyl-Substituted Allenes. Allenes are used for the reactions immediately after preparation because of their rapid polymerization (see the Experimental Section). Irradiation of a deaerated benzene solution (argon flush) containing 2,3-dichloro-1,4-naphthoquinone **1a** (0.04 M) and 1,1-diphenylallene **2f** (0.08 M) through an aqueous $CuSO_4$ filter (>320 nm) afforded a sole photoproduct **3f** in good yield (89%) in addition to the unreacted starting materials **1a** and **2f** after silica gel chromatography (run 6 in Table I and Scheme II). Under this condition quinone **1** is selectively excited, since absorption of the light by allene **2** is negligible. This reaction did not proceed thermally. The yield given above is based on consumed quinone. The structure of product **3f** was not straightforward from the spectroscopic data. The IR spectra of **3f** (1660 cm^{-1}) and the chemical shift (176.1 ppm) of the ^{13}C NMR spectra showed the existence of one carbonyl group. The parent peak in the mass spectra appeared at *m/e* 418, 420, 422, indicating that one molecule of **2f** combined with one molecule of **1a**. The 400-MHz ^1H NMR and the $^1H-^1H$ shift correlation in the two dimensional NMR spectroscopy (supplementary material) showed the presence of two fixed benzene rings and a rotationally free one (Figure 1; these assignments are indicated in the Experimental Section). Furthermore, the ^{13}C NMR spectrum showed the existence of one quaternary carbon (80.9 ppm), indicating the spirocyclic structure of **3f**. The structure of **3f** was unequivocally established by analogy of the result obtained by X-ray crystallographic investigation of **3g** (Experimental Section and supplementary material). The latter results are shown in Figure 2. The compound **3g** involves a spirocyclic structure in which the two fixed benzene rings are perpendicular each other. The present reaction is quite different from the photochemistry of halo-1,4-naphthoquinones with 1,1-diphenylethylene (Scheme I); in the latter case the substitution of the halogen atom by ethylenic group is the major reaction (ethylene adduct). In the former, however, formal [2 + 4] cycloaddition reaction of allene at the carbonyl group of quinone takes place in spite of its $\pi\pi^*$ triplet state. The product **3f** was obtained similarly in dichloromethane (53%) or in acetonitrile (33%; [**1a**] = 0.02 M, [**2f**] = 0.04 M), but none of it was obtained in methanol ([**1a**] = 0.01 M, [**2f**] = 0.02 M). In the reactions of **1a** with other 1,1-diphenylallenes **2d**, **2e**, and **2g**, the corresponding spiropyran adducts **3d** (25%), **3e** (61%), **3g** (85%) were ob-

---

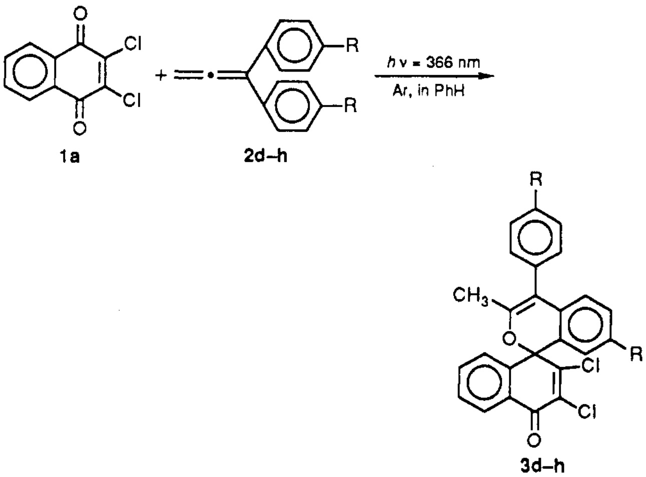
(19) Ogino, K.; Matsumoto, T.; Kawai, T.; Kozuka, S. *J. Org. Chem.* **1979**, *44*, 3352.

tained, respectively, but the photochemical reaction of **1a** with **2h** afforded no products in both benzene (run 11) and acetonitrile (run 12). The results are summarized in Scheme II and Table I.

In the reactions of other halo-1,4-naphthoquinones **1b** and **1c** with **2f** the similar spiropyran adducts **3i** (52%), and **3j** (33%) were obtained, respectively, but no products were obtained in the reaction of 1,4-naphthoquinone **1d** with **2f** (run 15). The regiochemistry of **3j** was determined as follows. The chemical shifts of the ^{13}C NMR spectrum showed a characteristic of α,β-unsaturated ketone. Since it was reported that in 2-chloro-2-cyclohexen-1-one a ^{13}C NMR signal due to C_3 appeared at 147.0 ppm, while in 3-chloro-2-cyclohexen-1-one that due to C_3 appeared at 158.1 ppm.[20] In **3j** the ^{13}C NMR signal due to C_2, which is determined by ^{13}C off-resonance NMR spectroscopy together with comparison with the ^{13}C NMR signals of **3f**, appeared at 141.1 ppm. Accordingly, the structure of **3j** was assigned to correspond to the former, assuming that other substituents do not affect appreciable influences on the halo-2-cyclohexen-1-one framework. In the reaction of chloranil **1e** with **2f**, only the reduction product of **1e**, hydroquinone **5** (50%), was produced (run 16). Interestingly, photochemical reaction of **1a** with 1,1-diphenyl-3-methylallene **2l** afforded chromene derivative **6** (45%). The parent peak in the mass spectra of **6** appeared at m/e 432, 434, 436, indicating that one molecule of **2l** had been incorporated into the **1a**. The IR spectra of the product **6** showed absorption at 3500 cm^{-1}, and the broad singlet at 5.76 ppm in the ^{1}H NMR spectra could be assigned to the phenolic hydroxyl group. The methyl protons (1.89 ppm as doublet) coupled with the proton (4.65 ppm as quartet). In the aromatic region, two protons (8.09 ppm, doublet; 7.47 ppm, triplet) and 11 protons (7.0–7.3 ppm) appeared. 1,1-(Diphenyl-d_{10})-3-methylallene (**2l′**) was prepared from bromobenzene-d_5 and ethyl propionate to assign the chemical shifts of ^{1}H NMR resonance in the aromatic region. The photochemical reaction of **ua** with 1,1-(diphenyl-d_{10})-3-methylallene (**2l′**) gave **6** with two benzene-d_5 rings (see the Experimental Section). Ten protons at 7.0–7.3 ppm disappeared and one proton remained at 7.04 ppm as a doublet in its ^{1}H NMR spectrum. This indicates the involvement of one proton (7.04 ppm, doublet), which is coupled to the proton that occurred at 7.47 ppm, in the 11 protons. The 2D Cosy NMR spectrum of **6** and the ^{13}C NMR spectrum (including ^{13}C off-resonance spectrum) also support the structure of **6** (Experimental Section and supplementary material). Furthermore, ozonolysis of **6** in methanol–dichloromethane gave polymerized products and benzophenone (15%), indicating the structure of **6**.

On the other hand, photochemical reactions of **1a** with 1-phenylallene **2a–c** gave not only spiropyran adducts **3b** and **3c**, but also [2 + 2] cyclobutane adducts **4a,b** (major isomer) and **4a′,b′** (minor isomer), which were the mixture of diastereomers in the ratio of 6:1 (run 1) or 4:1 (run 2). It is noteworthy that the reaction modes dramatically change with varying allene **2a–c**; in the reaction of **1a** with **2a**, **2c**, only cyclobutane adducts **4a**, **4a′** (74%), and spiropyran adduct **3c** (14%) were obtained, respectively, whereas in the reaction of **1a** with **2b** both cyclobutane adducts **4b**, **4b′** (66%), and spiropyran adduct **3b** (8%) were obtained. Spectroscopic analyses and comparison with **3d–g** confidently support the structural assignments of **3a,b**. On the other hand, these diastereomers **4a**, **4a′**, **4b**, and **4b′** were further separated by careful flash column chromatography. The structural assignments of the products were done straightforwardly by their spectra, though the configuration of **4a,b** and **4a′,b′** have not be determined. The parent peak in the mass spectrum of **4a** appeared at m/e 342, 344, 346, indicating that one molecule of **2a** had been incorporated into **1a**. Two carbonyl carbons appeared at 186.8, 187.8 ppm in the ^{13}C NMR spectrum. ^{13}C–^{1}H two-dimensional NMR spectroscopy (supplementary material) revealed the correlation between ^{1}H and ^{13}C NMR chemical shifts of methylenecyclobutane ring in **4a** (^{1}H vs ^{13}C (ppm): =CH$_2$, 5.49 and 5.98 vs 116.0; CHPh, 4.74 vs 57.4). The spectrscopic data of the minor isomer **4a′** is quite similar to that of the major isomer **4a**, indicating that **4a′** is the isomer of **4a**.

Table II. Photoreactivity of 2,3-Dichloro-1,4-naphthoquinone 1a with Para Disubstituted 1,1-Diphenylallenes 2d–h in Initial Stage



starting allene	product (rel quantum yield for 3d–′ vs 3f)^a
2d: R = F	**3d**: R = F (0.10)
2e: R = Cl	**3e**: R = Cl (0.10)
2f: R = H	**3f**: R = H (1.00)
2g: R = Me	**3g**: R = Me (0.64)
2h: R = OMe	**3h**: R = OMe (0)

[a] Relative quantum yields were measured by using ferrioxalate actinometer under 366-nm irradiation.

In the reaction of **1a** with triphenylallene **2m** (run 18) or tetraphenylallene **2n** (run 19), no photochemical reaction took place.

Mechanistic Studies. Photoreactivities of **1a** (0.01 M) with para-disubstituted 1,1-diphenylallenes **2d–h** (0.02 M) at the initial stages in benzene (366 nm) are summarized in Table II. Formation of the spiropyran adducts **3** were followed by 400-MHz NMR spectroscopy. Relative quantum yields compared with relative yield of **3f** in the reaction of **1a** with **f** were determined at less than 10% conversion, and within this limit formation of **3** increased linearly with irradiation time. In all cases except with allene **2h** spiropyran adducts were obtained. When the more electron-donating allenes such as **2f**, **2g** were subjected to the reaction, the values of relative quantum yields of **3f**, **3f**, were higher than those in the reactions with the more electron-accepting allenes such as **2d**, **2e**.

To clarify solvent dependency of the reaction a mixture of **1a** (0.01 M) and **2f** (0.02 M) was irradiated (>340 nm) in several solvents. The amount of **3f** produced in a initial stage was followed by 400-MHz NMR spectroscopy and was determined at conversion less than 10% (Table III). The relative yields (vs that in benzene) of the spiropyran derivatives in all solvents except with methanol increased

---

(20) Höfle, G. *Tetrahedron* **1976**, *32*, 1431.

Table III. Initial Stage Photoreactivity of 2,3-Dichloro-1,4-naphthoquinone (1a) with 1,1-Diphenylallene (2f) in Various Solvents

$$\mathbf{1a} + \mathbf{2f} \xrightarrow{h\nu > 340 \text{ nm, Ar}} \mathbf{3f}$$

solvent	E_T[a]	product (rel yield for the case in PhH)
PhH	34.5	1.0
CH_2Cl_2	41.1	1.4
MeCN	46.0	2.0
MeOH	55.5	0

[a] Dimroth's solvent parameter.

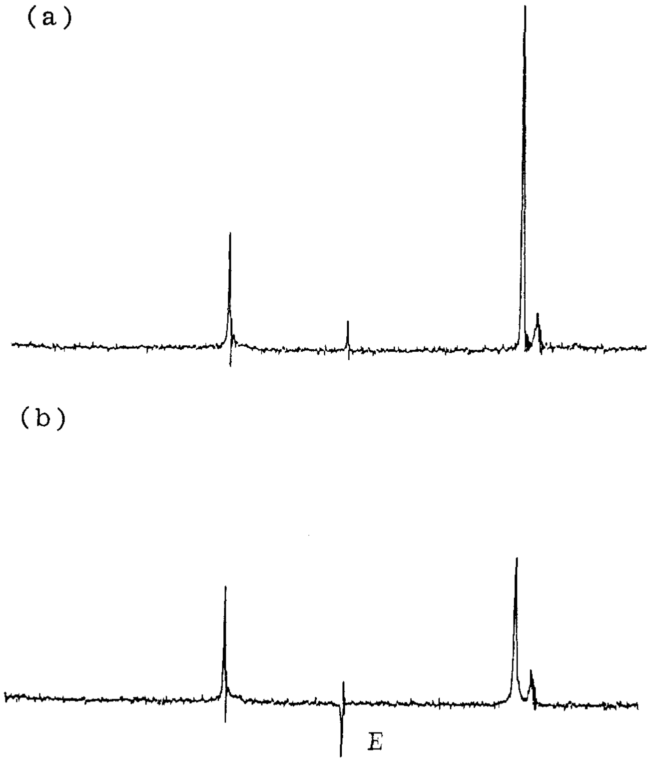


Figure 3. ^1H NMR spectra of acetonitrile-d_3 solution containing **1e** and **2f** (a) in the dark and (b) during irradiation.

slightly as the polarity of a solvent increased. It is noteworthy that in methanol the spiropyran adduct was not obtained.

CIDNP Studies. When an acetonitrile-d_3 solution of **1a** ($\sim 10^{-2}$ M) and **2f** ($\sim 10^{-2}$ M) was irradiated (>350 nm) under argon, strong ^1H CIDNP signal was observed, which was attributable to the methylene H of **2f**; the methylene H showed enhanced emission and other polarizations were weakened negligibly. On irradiation of an acetonitrile-d_3 solution containing **1e** and **2f** the similar but stronger ^1H CIDNP signal due to the methylene H of **2f** was observed[21] (Figure 3). The polarization pattern is similar to that observed in the photoreaction of **1a** with 1,1-diphenylethylene[2c] and is explainable by Kaptein's rule.[22] Electron transfer from **2f** to the excited triplet quinone **1a** generates an *ion radical pair in the triplet state* ($\mu > 0$). The reactants are regenerated by geminate electron return ($\epsilon > 0$). The *g* factor of the allene cation radical ($g = 2.002$–3)[23] is lower than that of the quinone anion radical ($g = 2.004$–5;[24] $\Delta g < 0$). Given these parameters, we can estimate the sign of hyperfine coupling constant. $\Gamma_{ne}(CH_2{=}) = \mu\epsilon(\Delta g)(a) = (+)(+)(-)(+) = -$ for **2f**. Thus, the sign of hyperfine coupling constant of methylene in **2f** is positive. It is known that allene cation radical $[C_3H_4]^{\bullet+}$ is a linear twisted species ($\sim 45°$).[10,11,13,15] On the other hand, Mariano reported that in 1,1-dimethylallene cation radical a linear species with less than 1°-twisting (shown in Figure 4) is the structure of minimum energy by ab initio calculations[15] because the cation radical generated is stabilized by alkyl substituents and as a result does not require twisting for further stabilization as predicted by Cederbaum on the basis of photoelectron spectroscopy data.[11] In our reactions, 1,1-diphenylallene cation radical stabilized by aryl substituents requires no twisting for stabilization. Thus, electron spin is primarily localized at C_2, whereas the charge is primarily localized in the diarylmethyl moiety (Figure 4). Considering the pseudo π orbital of methylene at C_3, the sign of the hyperfine coupling constant of methylene in **2f** is positive, which is consistent with the

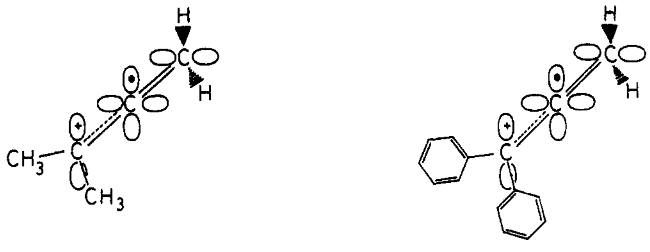


Figure 4. Structure of allene cation radical.

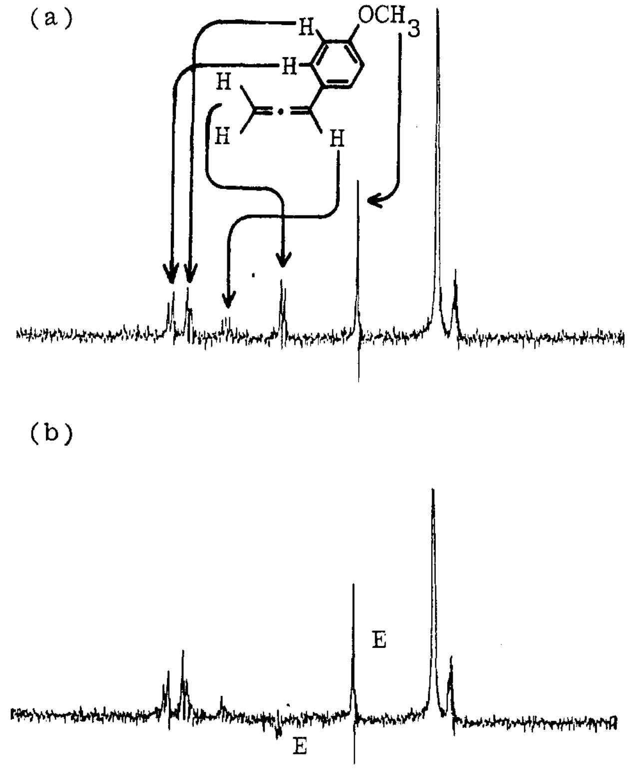


Figure 5. ^1H NMR spectra of acetonitrile-d_3 solution containing **1a** and **2c** (a) in the dark and (b) during irradiation.

---

[21] This case is analogous to that of Roth by which back electron transfer has been observed in the photoreaction of **1e** with various electron donors such as strained hydrocarbons. See: Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343 and references therein.

[22] Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732.

[23] Bolze, R.; Eierdauz, H.; Schlüter, K.; Massa, W.; Grahn, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 924.

[24] Fischer, H.; Hellwege, K.-H. *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Vol. 9, Magnetic Properties of Free Radicals*; Springer-Verlag: New York, 1980.

Table IV. Relationship between the Photoproducts and Redox Potentials[a]

quinone 1	$E_{1/2}(1^{\bullet-}/1)$, V	allene 2	$E_{1/2}(2/2^{\bullet+})$, V	E^T, kcal mol^{-1}	formation of 3 (or 6)	ΔG, kcal mol^{-1}
1a	−0.79	**2a**	1.42	56[b]	−	−5.0
		2b	1.23		+	−9.4
		2c	0.98		+	−15.2
		2d	1.25		+	−9.0
		2e	1.25		+	−9.0
		2f	1.20		+	−10.1
		2g	1.08		+	−12.9
		2h	0.85		−	−18.2
		2l	1.16		+	−11.0
		2m	1.20		−	−10.1
		2n	1.18		−	−10.6
1b	−0.79	**2f**		56[c]	+	−10.1
1c	−0.89	**2f**		56[c]	+	−7.8
1d	−1.06	**2f**		58[d]	−	−5.9
1e	−0.35	**2f**		62[e]	−	−26.3

[a] Obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (0.1 M) in acetonitrile solution vs Ag/0.1 M $AgClO_4$. [b] From our work.[6] [c] Assumed that the value of E^T is 56 kcal mol^{-1}. [d] From ref 1a. [e] From Kasha.[28]

CIDNP results. Furthermore, strong emission for the methylene H and no polarization in the aromatic rings support the linear nontwisted structure of cation radical $\mathbf{2f}^{\bullet+}$.[25] On the other hand, no polarizations were observed in benzene-d_6. Similar CIDNP signals in which the methylene H of reactant **2** were polarized (emission: $\Gamma_{ne}(CH_2{=}) = (+)(+)(-)(+) = -$ for **2d–h**) due to back electron transfer were observed when **1a** was irradiated in the presence of 1,1-diphenylallenes **2d–h** in acetonitrile-d_3,[26] and polarizations in electron-rich allenes were stronger than those in electron-poor allenes. Appreciable polarizations were not observed in benzene-d_6, similarly. In the reaction of **1a** with **2c**, polarization signals of reactant **2c** were observed in acetonitrile-d_3: the methylene H (strong emission) and methoxyl H showed emission, and other polarizations were negligibly small (Figure 5). These polarization signals due to the back electron transfer from $\mathbf{1a}^{\bullet-}$ to $\mathbf{2c}^{\bullet+}$ are also explained by Kaptein's rule: $\Gamma_{ne} = (+)(+)(-)(+) = -$ for methylene H and methoxyl H of **2c**. In benzene-d_6, however, none of the polarization signals were observed. Similarly, when **1a** was irradiated in the presence of **2b** CIDNP signals due to back electron transfer were observed in acetonitrile-d_3, but not in benzene-d_6: the methylene H and methyl H showed emission: $\Gamma_{ne} = (+)(+)(-)(+) = -$. However, in the reaction of **1a** with **2a** none of the polarization signals were observed in both benzene-d_6 and acetonitrile-d_3. In the reactions use of **1e** instead of **1a** afforded the similar and stronger CIDNP signal due to the back electron transfer.

Discussion

The free energy change (ΔG) in the photoinduced electron-transfer process between quinone **1** and allene **2** is given by the Rehm–Weller equation (1).[27] $E_{1/2}(2/2^{\bullet+})$

$$\Delta G(\text{kcal mol}^{-1}) = 23.06[E_{1/2}(2/2^{\bullet+}) - E_{1/2}(1^{\bullet-}/1) - e_c^2/a\epsilon] - E^T \quad (1)$$

is the oxidation potential of **2**, and $E_{1/2}(1^{\bullet-}/1)$ is the reduction potential of **1**, which were measured by cyclic voltammetry (Experimental Section). The Coulombic attraction term $e_o^2/a\epsilon$ is the energy gained by bringing the two ion radicals to the encounter distance "a" in a solvent of dielectric constant ϵ, and E^T is the triplet excitation energy of **1**. We assume that the Coulombic attraction term is negligible in the present reactions as long as discussion is confined to a series of related compounds.[3d] The reported or assumed values as the triplet excitation energies of **1a–e** are used.[1a,6,28] Equation 1 allows us to estimate ΔG for photoinduced electron transfer from **2** to **1** (Table IV). Actually in the photochemical reactions in which the calculated ΔG values were smaller than −7.8, the spiropyran adducts were obtained.[29]

Whether the spiropyran derivatives **3** are formed or not in the photoreactions of **1** with **2** depends not only upon the electron-donating ability of allenes **2** but also upon the electron-accepting ability of quinones **1**. Quinones **1a–c**, with the higher reduction potentials, form spiropyran adducts in the reactions with 1,1-diphenylallene **2f** (Table IV), while no products were obtained in the reaction of **1d** with low reduction potential. Futhermore, increase of the product **3** parallels with increasing reduction potential of quinone **1**. Quinone **1e** tends toward reduction itself because of the strong oxidizing power. In the reaction of **1a** with 1,1-diphenylallene **2d–h** increase of **3** or of the relative quantum yield of **3** in the initial stage parallels with the decrease of the oxidation potential of allene **2d–g** except with **2h**. These tendencies are consistent with the photoreaction of 1,1-diphenylethylene with quinone in which increase of electron-donating character of the ethylene favors ethylene adduct formation.[30] In electron-transfer photochemistry it is known that product formation was suppressed in the reaction of acceptor and donor having a p-methoxylaryl group.[3] None of **3h** was formed in both benzene and acetonitrile. Probably cation radical $\mathbf{2h}^{\bullet+}$ whose positive charge localizes upon methoxyl group became less reactive because of its stabilization. In the reaction of **1a** with phenylallenes **2a–c**, dramatic change of product formation was observed. That is, in the reaction of **1a** with **2a** only cyclobutane adduct was formed, while in the reaction of **1a** with **2b** both cyclobutane and spiropyran adducts were formed, and in the reaction of **1a**

---

[25] Similar CIDNP effects were observed by Roth. Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079.

[26] In the photoreactions of **1a** with **2d**, **2e**, **2g**, and **2h** other polarizations were negligible except the case of **2h** in which emission signal due to the methoxyl group was observed. $\Gamma_{ne}(OCH_3) = (+)(+)(-)(+) = -$ for **2h**.

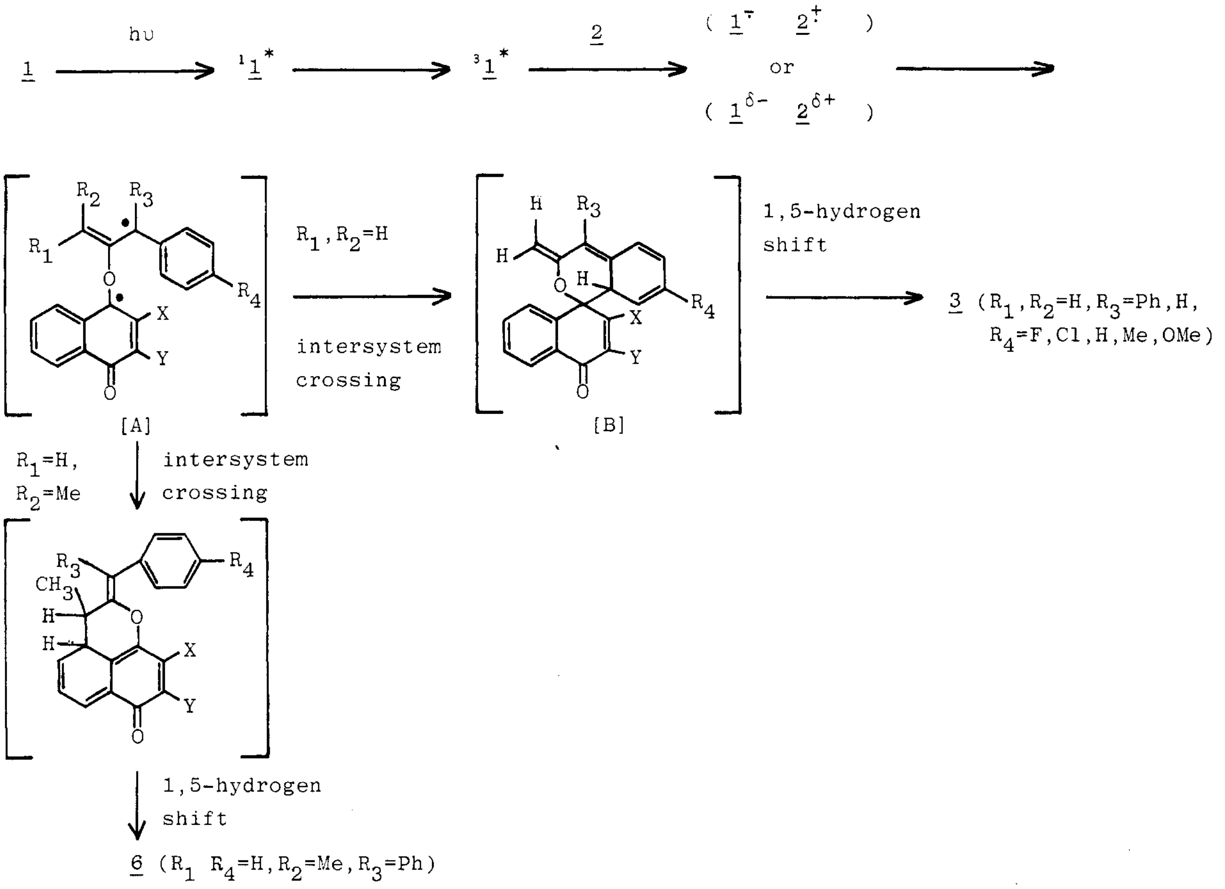
[27] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[28] Kasha, M. *Chem. Rev.* **1947**, *41*, 401.

[29] Although the calculated ΔG had a negative value in all cases, spiropyran adduct was not formed in some cases (run 1 and run 15 in Table I). In this case, the actual ΔG may be positive, probably because of the large contribution of Coulombic term.

[30] Quantum yield of ethylene adduct formation in the photoreaction of **1a** with 1,1-bis(4-methoxyphenyl)ethylene is also lower than that in the reaction of **1a** with 1,1-diphenylethylene.[2c]

Scheme III



with **2c** only spiropyran adduct was formed. Cyclobutane formation is well known in the reactions of substituted 1,4-naphthoquinone with alkyl- or arylethylenes[31] and also occurs in the reaction of duroquinone with 1,1-dimethylallene.[19] Dependence of the reaction course on the ΔG values of the electron transfer has been observed in many cases,[3d] and these results are consistent with those in quinone–1,1-diphenylethylene systems.[2c] Interestingly, the spiropyran adduct was obtained in the reaction of **2c**, but not in that of **2h**, though both allenes have a *p*-methoxylaryl group. However, the low yield of **3c** in spite of its high oxidation potential of **2c** seems to reflect the positive charge localization in the methoxyl group. These inclinations indicate that the value of ΔG correlates well with spiropyran adduct formation. On the other hand, none of the products were obtained in the photoreaction of **1a** with **2m** or **2n**, although large values of $-\Delta G$ indicate that electron transfer is possible. It is known that there is a tendency that values of excited triplet energy E^T of phenyl-substituted ethylene generally decrease with increasing conjugation.[32] Thus, excited triplet quinone (E^T = 50–60 kcal mol^{-1}) is quenched by allene **2m**, **2n** (E^T = 57 kcal mol^{-1} for **2n**[33]) having a lower triplet energy due to increased conjugation by the phenyl group, while no energy transfer occurs between excited triplet quinone and mono- or diphenylallene having a higher triplet energy (E^T > 60 kcal mol^{-1}).

Appreciable solvent effects were not observed in the reaction of **1a** with **2f** even in the initial stage except with that in the case of methanol. We have reported that in the reaction of **1a** with 1,1-diphenylethylene, use of a highly polar solvent suppresses ethylene adduct formation.[2c] In this case we could not observe similar inclination except within the reaction in methanol.[2c] Although the rate of formation of [A] probably decreases with increasing solvent polarity similar to the quinone–1,1-diphenylethylene system, the rates of formation of [B] and **3** are little dependent on the polarity of solvent (Scheme III). Accordingly, relative yields of **3f** are almost constant against solvent polarity since the rate-determining step may be the formation of [B] or **3**. Formation of [A] in methanol is suppressed similar to the ethylene adduct formation in methanol; thus, **3f** was not obtained.

Support of an electron-transfer mechanism for quinone–allene photoadditions comes from the CIDNP studies. The CIDNP results are consistent with the case of **1** with 1,1-diphenylethylene in which back electron transfer was observed in polar solvent, but not in nonpolar solvent.[2c] These CIDNP signals clearly indicate that the photoinduced electron transfer from **2** to **1** generates an ion radical pair, which in turn regenerates **1** and **2** via back electron transfer. CIDNP signals could not be detected in nonpolar solvent such as benzene-d_6. Appearance of the strong CIDNP signals requires a suitable distance (ca. 9 Å) between anion radical and cation radical and a certain lifetime in the ion radical pair.[32] In the nonpolar solvents such as benzene, the distance between the two radical species may be smaller because of the weak solvation, and the lifetime of the ion radical pair may be shorter (>10×) than those in polar solvents. In polar solvent the quinone anion radical and the allene cation radical could be drawn apart (ca. 9 Å) to the extent that they have enough lifetime

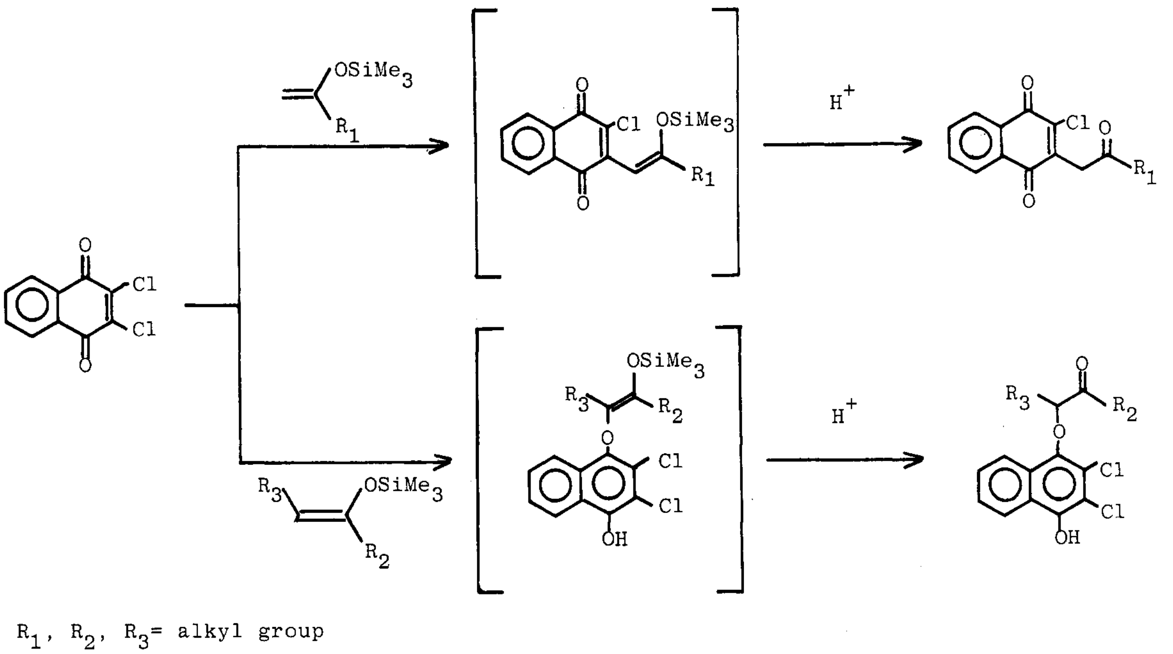
---

(31) (a) Otsuki, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2596. (b) Maruyama, K.; Narita, T. *Ibid.* **1980**, *53*, 757. (c) Ochiai, M.; Arimoto, M.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1981**, 460. (d) Liu, H. J.; Chan, W. H. *Can. J. Chem.* **1980**, *58*, 2196.

(32) Turro, N. J. In *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1978.

(33) Ullman, E. F.; Henderson, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 4390.

Scheme IV



R_1, R_2, R_3= alkyl group

to result in the CIDNP effects. However, we believe that even in polar solvents such as acetonitrile and methanol, back electron transfer is much faster than solvation to the ion pair, and the ion radical pair is not sufficiently dissociated to form a solvated ion pair under our conditions.[34]

Since a broad electronic absorption (maximum at 382 nm, absorbance 0.29) attributable to a charge-transfer (CT) complex was observed in a benzene solution of **1a** (0.002 M) and a large amount of **2f** (0.075 M), the possibility of a reaction path from the photoinduced CT complex could not be excluded. The weak CT complex could not be excited directly because the strong quinone absorption overlapped with the CT absorption. However, under our conditions extremely large absorption of quinone relative to CT absorption warrants the major reaction path initiated by direct excitation of quinone.

There are indications from several laboratories insisting that biradical intermediates, formed via an excited-state complex of a carbonyl compound with an alkene, is participating in oxetan formation reaction.[35] Wilson has shown that during the photooxetan formation in the reactions of *p*-quinone with alkenes, 1,4-biradicals may be produced via an excited-state complex.[36] Hammond reported that aliphatic and aromatic ketones photochemically react to allenes to form oxetane via probably 1,4-biradical.[37] We propose an electron-transfer mechanism shown in Scheme III.[38] The excited triplet quinone reacts with allene to make an ion radical pair via electron transfer, although, instead, an exciplex may be in nonpolar solvents such as benzene.[39] It is known that nucleophilic addition occurs to the central carbon C_2 of allene cation radical.[12,14-15] The close correspondence between the 1,1-diphenylallene linear 0°-twisted cation radical and that derived from 1,1-diphenylethylene suggests that nucleophilic addition should occur at the central carbon of allene cation radical because of steric effects.[15,16] Monophenylallene cation radical also seems to have linear 0°-twisted structure due to stabilization of the phenyl ring. Thus, addition of nucleophile, which in this case is a carbonyl oxygen in the quinone anion radical, to the allene cation radical would occur at C_2 to yield a 1,4-biradical intermediate due to steric effects as seen in the Paterno–Büchi reaction, although addition of the methylene group of cation radical in 1,1-diphenylethylene to the quinone anion radical occurs at C_2 or C_3 attached with halogen atom to yield ethylene adduct. In our earlier studies, we have found that photoreaction of halo-1,4-naphthoquinone with 2-alkoxy-1-alkenes such as 2-methoxy-1-alkene[4] and 2-(trimethylsiloxy)-1-alkene[5] afforded 2-(2-oxoalkyl)-1,4-naphthoquinone via ethylene adduct. Furthermore, orientation in the photoreaction of **1a** with silyl enol ether depends on the substitution mode of silyl enol ether[5] (Scheme IV): introduction of alkyl group into the ethylene moiety of 2-(trimethylsiloxy)-1-alkene resulted in the formation of naphthol derivatives (O-adduct), probably due to the steric hinderance between the halogen atom of the quinone anion radical and alkyl group R_3 of the alkene cation radical. These data suggest that selectivity of quinone anion radical attack toward ethylene or allene cation radical is strongly dependent on the nature of ethylene or allene in addition to the steric factor between radical pair. Biradical ([A] in Scheme III) stabilized by spin delocalization on the allene's phenyl rings could be stabilized finally by bond formation between the ketyl radical center of quinone moiety and the allene radical center via intersystem crossing to give intermediate [B]. Subsequently, this intermediate [B][40] would lead to the

---

[34] Radical cation produced in polar solvent can be trapped as a methanol or cyanide adduct.[16] Johnson and Mariano reported that methanol adducts were obtained in allene-derived electron-transfer photochemistry.[14,15] Under our condition, similar adduct could not be detected in methanol. Similar results were obtained by us[2c] and Mattay.[3d]

[35] Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549. Gupta, A.; Hammond, G. S. *J. Am. Chem. Soc.* **1976**, *98*, 1218. Yang, N. C.; Hui, M. H.; Shod, D. M.; Turro, N. J.; Hautala, R. R. Dawes, K.; Dalton, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3023.

[36] Wilson, R. M.; Musser, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1720.

[37] Gotthardt, H.; Steinmetz, R.; Hammond, G. S. *J. Org. Chem.* **1968**, *33*, 2774.

[38] Electron-transfer processes have recently been shown to occur as well in the photoreaction of ketone and electron-rich allene.[3d]

[39] Neither fluorescence spectra of **1a** nor exciplex emission spectra in a mixture of **1a** with **2f** could be observed. Because of the high efficiency of intersystem crossing ($S_1 \rightarrow T_1$) in the excited state of quinone,[1a] we can assume that this reaction proceeds via excited triplet state.

[40] This intermediate was not isolated nor could it be detected by standard analytical means.

spiropyran adduct via a 1,5-hydrogen shift.[41] Regioselective formation of **3j** may be due to the steric repulsion between chlorine atom and allene together with the negative charge density of two oxygen atoms of anion radical of **1c**. Barltrop and Hesp reported[42] that main products upon irradiation of *p*-quinone and acyclic dienes were spiropyrans, and these compounds are related closely to our cases. Interestingly 1,1-diphenyl-3-methylallene gave a chromene derivative. Introduction of a methyl group to 1,1-diphenylallene changes the stabilization of the biradical which coupled between C_3 in allene and phenyl ring of quinone, and subsequently **6** was produced after 1,5-hydrogen shift (Scheme III).[43] These experimental results suggest that the substitution mode of allenes could be the controlling factor of the reaction course.

In conclusion, photochemical reaction of halo-1,4-naphthoquinone with monophenylallene or 1,1-diphenylallene afforded the [2 + 4] cycloadduct between the carbonyl group of quinone and allene, whereas the substituted adduct of a halogen atom by an ethylenic group was obtained in the photoreaction of halo-1,4-naphthoquinone with 1,1-diphenylethylene. The two reactions are very similar in their outlook but are greatly different in the solvent effects as well as their insight of the reactions initiated by photoinduced electron transfer.

Experimental Section

General Methods. All melting points were determined with a Yanagimoto micro-melting apparatus and uncorrected. Mass spectra (high resolution and low resolution) were taken on a JEOL JMS-DX300 mass spectrometer. The electronic spectra were obtained by using a Shimadzu UV-100 spectrometer. ^{1}H NMR spectra were recorded by using a JEOL PS-100 or a JEOL DX-400 spectrometer. Spectra were obtained in deuteriochloroform or carbon tetrachloride as a solvent, and chemical shifts were recorded in parts per million (ppm) on the δ scale from tetramethylsilane as an internal standard. ^{13}C NMR spectra and 2D Cosy NMR spectra were recorded by using a JEOL DX-400 spectrometer. IR spectra were obtained by using a JASCO IRA-1 spectrometer on KBr pellets. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Starting Materials. 2,3-Dichloro-1,4-naphthoquinone (**1a**), 1,4-naphthoquinone (**1d**), and chloranil (**1e**) were commercially available from Nacalai Tesque Co. or Wakenyaku Co. and used after recrystallization. 2,3-Dibromo-1,4-naphthoquinone (**1b**)[44] and 2-chloro-1,4-naphthoquinone (**1c**)[45] were synthesized according to methods described in the literature. 1,1-Diphenylallenes **2d–h**,[46] 1,1-diphenyl-3-methylallene (**2l**),[46] and 1,1-(diphenyl-d_{10})-3-methylallene (**2l′**)[46] were prepared from the corresponding 1,1-diphenylethylene derivatives by the methods given in the references and immediately used after column chromatography. Triphenylallene (**2m**) was prepared according to the methods given in the ref 47 and immediately used after column chromatography. Phenylallenes **2a–c**[48] were prepared according to the reported methods and used after distillation. Tetraphenylallene (**2n**)[49] was prepared according to the reported method and used after recrystallization. The synthesis of 1,1-(diphenyl-d_{10})-1-propane (>99% D) was carried out by treatment of Grignard reagent (from bromobenzene-d_5 (>99% D)) with ethyl propionate followed by dehydration in dimethyl sulfoxide.

Preparation of 1,1-Diphenylcyclopropane.[46] A mixture of potassium *tert*-butoxide (18.0 g, 0.16 mol), 1,1-bis(4-fluorophenyl)ethylenes (8.6 g, 0.04 mol), and dry hexane (100 mL) was cooled in an ice–salt bath. Bromoform (15.2 g, 0.06 mol) was added dropwise with stirring during 0.5 h. The reaction mixture was left at room temperature overnight. Water was added, and the product was extracted with ether. The aqueous phase was extracted with ether, and the combined extract was washed with water until neutral, dried over sodium sulfate, and concentrated in vacuo. Recrystallization from ethanol gave 8.1 g (52%) of 1,1-dibromo-2,2-bis(4-fluorophenyl)cyclopropane: white crystals; mp 126–129 °C; MS *m/e* 386, 388, 390 (M^+); IR (KBr) 1590, 1480, 1420, 1210, 820 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.43 (2 H, s), 7.03 (4 H, m), 7.48 (4 H, m). Anal. Found: C, 46.30; H, 2.58; F, 9.85; Br, 41.24. Calcd for $C_{15}H_{10}F_2Br_2$: C, 46.43; H, 2.60; F, 9.79; Br, 41.18.

1,1-Bis(4-chlorophenyl)-2,2-dibromocyclopropane was prepared from 1,1-bis(4-chlorophenyl)ethylene in 45% yield: white crystals; mp 138–141 °C; MS *m/e* 418, 420, 422, 424, 426 (M^+); IR (KBr) 1470, 1420, 1390, 1080, 990, 820 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.41 (2 H, s), 7.1–7.5 (8 H, m). Anal. Found: C, 42.88; H, 2.25; Cl, 16.74; Br, 37.73. Calcd for $C_{15}H_{10}Cl_2Br_2$: C, 42.80; H, 2.39; Cl, 16.84; Br, 37.96.

1,1-Dibromo-2,2-bis(4-methylphenyl)cyclopropane was prepared from 1,1-bis(4-methylphenyl)ethylene in 35% yield: white crystals; mp 127–130 °C; MS *m/e* 378, 380, 382 (M^+); IR (KBr) 1510, 1420, 820, 720 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.32 (6 H, s), 2.38 (2 H, s), 7.11 (4 H, d, J = 8 Hz), 7.39 (4 H, d, J = 8 Hz). Anal. Found: C, 53.71; H, 4.25; Br, 41.77. Calcd for $C_{17}H_{16}Br_2$: C, 53.72; H, 4.24; Br, 42.04.

1,1-Dibromo-2,2-bis(4-methoxyphenyl)cyclopropane was prepared from 1,1-bis(4-methoxyphenyl)ethylene in 30% yield: white crystals; mp 167–170 °C; MS *m/e* 410, 412, 414 (M^+); IR (KBr) 1600, 1510, 1450, 1240, 1020, 830 cm^{-1}; ^{1}H NMR (CCl_4) δ 2.35 (2 H, s), 3.79 (6 H, s), 6.79 (4 H, d, J = 9 Hz), 7.37 (4 H, d, J = 9 Hz). Anal. Found: C, 49.78; H, 3.83; Br, 38.71. Calcd for $C_{17}H_{16}O_2Br_2$: C, 49.55; H, 3.91; Br, 38.78.

1,1-Dibromo-2,2-diphenyl-3-methylcyclopropane was prepared from 1,1-diphenyl-1-propene in 71% yield: white crystals; mp 85–88 °C; MS *m/e* 364, 366, 368 (M^+); IR (KBr) 1590, 1480, 1440, 750, 690 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.31 (3 H, d, J = 7 Hz), 2.41 (1 H, q, J = 7 Hz), 7.0–7.4 (10 H, m). Anal. Found: C, 52.29; H, 3.90; Br, 43.63. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.85; Br, 43.65.

1,1-Dibromo-2,2-(diphenyl-d_{10})-3-methylcyclopropane (>99% D) was prepared from 1,1-(diphenyl-d_{10})-1-propene in 55% yield: white crystals; mp 70–73 °C; MS *m/e* 374, 376, 378 (M^+); IR (KBr) 1560, 1430, 1380, 1320, 810, 750 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.31 (3 H, d, J = 7 Hz), 2.41 (1 H, q, J = 7 Hz).

Preparation of 1,1-Diphenylallenes.[46] 1,1-Dibromo-2,2-bis(4-fluorophenyl)cyclopropane (5.0 mmol) was diluted with 20 mL of dry ether and cooled in a dry ice/acetone bath kept at −30 to −40 °C. An ethereal solution of methyllithium (6.0 mmol) was added dropwise with stirring during 10 min. The reaction mixture was further stirred for 30 min, and then water was added. The ether layer was separated, and the aqueous phase was extracted with a small amount of ether. The combined ether solutions were washed with water until neutral and dried over sodium sulfate. Solvents were removed in vacuo, and the reaction mixture was separated by flash column chromatography (hexane), affording 510 mg (45%) of **2d**: white crystals from hexane–dichloromethane; mp 62–65 °C; high resolution mass spectrum, found 228.0755, calcd for $C_{15}H_{10}F_2$ 228.0750; IR (NaCl) 1940, 850 (C=C=C) cm^{-1}; ^{1}H NMR (CCl_4) δ 5.20 (2 H, s), 6.98 (4 H, m), 7.23 (4 H, m).

1,1-Bis(4-methylphenyl)allene (2g): yield 44%; white crystals from hexane–dichloromethane; mp 68–72 °C; high-resolution mass spectrum, found 220.1249, calcd for $C_{17}H_{16}$ 220.1251; IR (NaCl) 1930, 840 (C=C=C) cm^{-1}; ^{1}H NMR (CCl_4) δ 2.35 (6 H, s), 5.16 (2 H, s), 7.04 (4 H, d, J = 8 Hz), 7.17 (4 H, d, J = 8 Hz).

1,1-Bis(4-methoxyphenyl)allene (2h): yield 60%; white crystals from hexane–dichloromethane; mp 95–98 °C; high-resolution mass spectrum, found 252.1146, calcd for $C_{17}H_{16}O_2$ 252.1149; IR (NaCl) 1930, 840 (C=C=C) cm^{-1}; ^{1}H NMR (CCl_4) δ 3.83 (6 H, s), 5.21 (2 H, s), 6.93 (4 H, d, J = 9 Hz), 7.33 (4 H, d, J = 9 Hz).

---

(41) Origin of a proton of methyl group in **3** could not be determined by the preliminary experiment of the labeled 1,1-diphenylallene or labeled solvents.

(42) Barltrop, J. A.; Hesp, B. *J. Chem. Soc. C* **1967**, 1625.

(43) Similar photocyclizations were observed in the photoreaction of xanthenthione with allene. Kamphuis, J.; Hupkes, J. G.; Visser, R. G.; Bos, H. J. T. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 114.

(44) Zincke, T.; Schmidt, M. *Chem. Ber.* **1894**, *27*, 2758.

(45) Cleve, P. T. *Chem. Ber.* **1890**, *23*, 954.

(46) Skattebol, L. *Acta Chem. Scand.* **1963**, *17*, 1683.

(47) Cram, D. J.; Willey, F.; Fischer, H. P.; Relles, H. M.; Scott, D. A. *J. Am. Chem. Soc.* **1966**, *88*, 2759.

(48) Moreau, J. L.; Gaudemar, M. *J. Organomet. Chem.* **1976**, *108*, 159.

(49) Tadros, W.; Sakla, A. B.; Helmy, A. A. A. *J. Chem. Soc.* **1961**, 2687.

1,1-Diphenyl-3-methylallene (2l): yield 40%; colorless oil; high-resolution mass spectrum, found 206.1090, calcd for $C_{16}H_{14}$ 206.1095; IR (NaCl) 1920, 850 (C=C=C) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.86 (3 H, d, J = 7 Hz), 5.58 (1 H, q, J = 7 Hz), 7.21 (10 H, m).

1,1-(Diphenyl-*d*$_{10}$)-3-methylallene (2l′): yield 37%; colorless oil; high-resolution mass spectrum, found 216.1720, calcd for $C_{16}H_4D_{10}$ 216.1723; IR (NaCl) 1920, 850 (C=C=C) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.86 (3 H, d, J = 7 Hz), 5.58 (1 H, q, J = 7 Hz), 7.21. Integration of the NMR spectrum indicated that deuterium incorporation was >95%.

General Procedure for the Preparative Photochemical Reaction. A benzene solution (25 mL in a Pyrex tube) of **1** (1 mmol) and **2** (2 mmol) was irradiated through an aqueous $CuSO_4$ filter for 3 h at room temperature with a high-pressure Hg lamp (300 W). After irradiation, the reaction mixture was concentrated in vacuo and separated by flash column chromatography on silica gel (Merck Keisel gel 60H), developing with hexane–benzene (3:1), benzene subsequently, and chloroform finally. The first band contains unreacted allene, the second one contains spiropyran adduct **3** (or **6**), the third one contains unreacted quinone **1**, and the final one contains cyclobutane adduct **4** (or **5**). These products are identified by the following spectroscopic data.

Physical Properties of the Products. 4,8-Dimethyl-2*H*-benzo[*c*]pyran-2-spiro-1′-(2′,3′-dichloro-4′-oxo-1′,4′-dihydronaphthalene) (3b): yellow crystals from hexane–chloroform; mp 189–191 °C; MS *m*/*e* 356, 358, 360 (M$^+$); IR (KBr) 1650 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.97 (3 H, s), 2.10 (3 H, s), 5.55 (1 H, s), 6.24 (1 H, s), 6.88 (1 H, d, J = 7.9 Hz), 6.96 (1 H, d, J = 8.5 Hz), 7.47 (1 H, td, J = 8.0, 1.8 Hz), 7.5–7.6 (2 H, m), 8.19 (1 H, d, J = 7.9 Hz). Anal. Found: C, 66.97; H, 4.03; Cl, 19.89. Calcd for $C_{20}H_{14}O_2Cl_2$: C, 67.24; H, 3.95; Cl, 19.85.

4-Methoxy-8-methyl-2*H*-benzo[*c*]pyran-2-spiro-1′-(2′,3′-dichloro-4′-oxo-1′,4′-dihydronaphthalene) (3c): yellow needles from hexane–chloroform; mp 165–167 °C; MS *m*/*e* 372, 374, 376 (M$^+$); IR (KBr) 1640 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.95 (3 H, s), 3.58 (3 H, s), 5.54 (1 H, s), 6.03 (1 H, s), 6.70 (1 H, d, J = 8.3 Hz), 6.93 (1 H, d, J = 8.6 Hz), 7.44 (1 H, t, J = 8.5 Hz), 7.5–7.6 (2 H, m), 8.16 (1 H, d, J = 7.6 Hz). Anal. Found: C, 64.54; H, 3.74; Cl, 19.03. Calcd for $C_{20}H_{14}O_3Cl_2$: C, 64.36; H, 3.78; Cl, 19.00.

4-Fluoro-7-(4-fluorophenyl)-8-methyl-2*H*-benzo[*c*]pyran-2-spiro-1′-(2′,3′-dichloro-4′-oxo-1′,4′-dihydronaphthalene) (3d): yellow needles from hexane–dichloromethane; mp 190–192 °C; MS *m*/*e* 454, 456, 458 (M$^+$); IR (KBr) 1640 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.82 (3 H, s), 6.21 (1 H, dd, J = 8.4, 2.8 Hz), 6.63 (1 H, dd, J = 8.8, 5.5 Hz), 6.79 (1 H, td, J = 8.2, 2.5 Hz), 6.9–7.3 (4 H, m, Ph), 7.54 (1 H, td, J = 6.7, 1.8 Hz), 7.65 (2 H, m), 8.24 (1 H, dd, J = 8.6, 3.0 Hz). Anal. Found: C, 65.91; H, 3.31; F, 8.34; Cl, 15.62. Calcd for $C_{25}H_{14}O_2F_2Cl_2$: C, 65.95; H, 3.10; F, 8.35; Cl, 15.57.

4-Chloro-7-(4-chlorophenyl)-8-methyl-2*H*-benzo[*c*]pyran-2-spiro-1′-(2′,3′-dichloro-4′-oxo-1′,4′-dihydronaphthalene) (3e): yellow crystals from dichloromethane–methanol; mp 188–191 °C; MS *m*/*e* 486, 488, 490, 492, 494 (M$^+$); IR (KBr) 1650 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.83 (3 H, s), 6.45 (1 H, d, J = 2.1 Hz), 6.60 (1 H, d, J = 8.5 Hz), 6.91 (2 H, d, J = 8.8 Hz), 7.19 (2 H, d, J = 8.8 Hz), 7.64 (1 H, dd, J = 8.5, 2.1 Hz), 7.54 (1 H, t, J = 8.3 Hz), 7.61 (1 H, t, J = 8.3 Hz), 7.68 (1 H, d, J = 7.6 Hz), 8.24 (1 H, d, J = 7.9 Hz). Anal. Found: C, 61.21; H, 2.86; Cl, 29.29. Calcd for $C_{25}H_{14}O_2Cl_4$: C, 61.51; H, 2.89; Cl, 29.05.

8-Methyl-7-phenyl-2*H*-benzo[*c*]pyran-2-spiro-1′-(2′,3′-dichloro-4′-oxo-1′,4′-dihydronaphthalene) (3f): yellow cubics from hexane–chloroform; mp 171.5–173 °C; MS *m*/*e* 418, 420, 422 (M$^+$); IR (KBr) 1660 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84 (3 H, s, CH_3), 6.49 (1 H, d, J = 7.4 Hz, H_e), 6.68 (1 H, d, J = 7.6 Hz, H_h), 6.94 (1 H, t, J = 7.4 Hz, H_f), 7.07 (1 H, t, J = 7.0 Hz, H_g), 7.3–7.5 (5 H, m, Ph), 7.51 (1 H, t, J = 7.0 Hz, H_b), 7.64 (1 H, t, J = 7.8 Hz, H_c), 7.69 (1 H, d, J = 7.6 Hz, H_d), 8.22 (1 H, d, J = 7.3 Hz, H_a) (These assignments in the ^{1}H NMR spectrum of **3f** were done by 2D Cosy ^{1}H NMR spectroscopy and comparison with those of **3a–e**); ^{13}C NMR ($CDCl_3$) δ 18.2, 80.9, 100.4, 110.1, 123.8, 125.4, 126.4, 126.6, 126.8, 127.2, 127.8, 128.1, 128.6, 128.7, 129.0, 129.2, 129.9, 130.8, 131.4, 134.2, 136.1, 146.3, 148.4, 176.1. Anal. Found: C, 71.59; H, 3.87; Cl, 16.76. Calcd for $C_{25}H_{16}O_2Cl_2$: C, 71.61; H, 3.85; Cl, 16.91.

4,8-Dimethyl-7-(4-methylphenyl)-2*H*-benzo[*c*]pyran-2-spiro-1′-(2′,3′-dichloro-4′-oxo-1′,4′-dihydronaphthalene) (3g): yellow cubics from hexane–chloroform; mp 188–190 °C; MS *m*/*e* 446, 448, 450 (M$^+$); IR (KBr) 1670 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.82 (3 H, s), 2.08 (3 H, s), 2.42 (3 H, s), 6.27 (1 H, s), 6.60 (1 H, d, J = 8.2 Hz), 6.86 (1 H, d, J = 8.0 Hz), 6.9–7.3 (4 H, m), 7.49 (1 H, td, J = 8.0, 1.2 Hz), 7.61 (1 H, td, J = 7.0, 1.5 Hz), 7.67 (1 H, dd, J = 8.0, 1.0 Hz), 8.22 (1 H, dd, J = 8.0, 1.2 Hz). Anal. Found: C, 72.72; H, 4.49; Cl, 15.98. Calcd for $C_{27}H_{20}O_2Cl_2$: C, 72.49; H, 4.51; Cl, 15.85.

8-Methyl-7-phenyl-2*H*-benzo[*c*]pyran-2-spiro-1′-(2′,3′-dibromo-4′-oxo-1′,4′-dihydronaphthalene) (3i): yellow crystals from hexane–chloroform; mp 191–193 °C; MS *m*/*e* 506, 508, 510 (M$^+$); IR (KBr) 1660 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.85 (3 H, s), 6.50 (1 H, dd, J = 7.9, 1.2 Hz) 6.67 (1 H, d, J = 7.9 Hz), 6.93 (1 H, td, J = 7.6, 1.2 Hz)8 7.07 (1 H, td, J = 7.6, 1.2 Hz), 7.3–7.4 (2 H, m), 7.4 (1 H, m), 7.4–7.6 (3 H, m), 7.61 (1 H, td, J = 7.3, 1.5 Hz), 7.69 (1 H, dd, J = 7.9, 0.9 Hz), 8.21 (1 H, dd, J = 7.6, 1.2 Hz).

8-Methyl-7-phenyl-2*H*-benzo[*c*]pyran-2-spiro-1′-(3′-chloro-4′-oxo-1′,4′-dihydronaphthalene) (3j): yellow crystals from methanol; mp 145–148 °C; MS *m*/*e* 384, 386 (M$^+$); IR (KBr) 1675 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.88 (3 H, s), 6.34 (1 H, d, J = 6.7 Hz) 6.69 (1 H, d, J = 8.0 Hz), 6.96 (1 H, td, J = 7.0, 1.2 Hz), 7.11 (1 H, td, J ='7.6, 1.5 Hz), 7.3–7.5 (5 H, m), 7.59 (1 H, td, J = 7.3, 1.2 Hz), 7.69 (1 H, td, J = 7.3, 1.5 Hz), 7.70 (1 H, s), 7.81 (1 H, d, J = 7.0 Hz), 8.28 (1 H, dd, J = 8.2, 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 18.0, 77.4, 114.0, 123.3, 124.8, 126.8, 126.9, 127.3, 128.6, 128.8, 129.1, 129.2, 130.2, 130.8, 131.2, 132.4, 133.7, 135.9, 141.1 ($C_{2'}$), 143.6, 148.1, 177.4. Anal. Found: C, 77.94; H, 4.23; Cl, 9.30. Calcd for $C_{25}H_{17}O_2Cl$: C, 78.02; H, 4.45; Cl, 9.21.

The diastereomer mixture of **4a**, **4a′** (6:1) was separated by flash column chromatography (hexane–ether–2-propanol, 200:5:1). The former band contains **4a′** and the latter one contains **4a**.

3,4-Benzo-1,6-dichloro-7-methylene-8-phenylbicyclo-[4.2.0]oct-3-ene-2,5-dione. Major isomer (4a): white crystals from methanol; mp 122–124 °C; MS *m*/*e* 342, 344, 346 (M$^+$); IR (KBr) 1680 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.74 (1 H, m), 5.49 (1 H, m), 5.98 (1 H, m), 7.2–7.4 (5 H, m), 7.90 (2 H, m), 8.26 (2 H, m); ^{13}C NMR ($CDCl_3$) δ 57.4 (d), 72.9 (q), 76.1 (q)8, 116.0 (t), 128.2 (d), 128.4 (d), 128.6 (d)8 128.7 (d), 129.5 (d), 132.5 (s), 132.6 (s)8, 133.0 (s), 135.2 (d), 135.5 (d), 143.2 (s), 186.8 (s), 187.8 (s). Anal. Found: C, 66.29; H, 3.35; Cl, 20.86. Calcd for $C_{19}H_{12}O_2Cl_2$: C, 66.49; H, 3.52; Cl, 20.66.

Minor isomer (4a′): white crystals from chloroform–methanol; mp 116–119 °C; MS *m*/*e* 342, 344, 346 (M$^+$). IR (KBr) 1680 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.15 (1 H, m), 5.42 (1 H, m), 5.71 (1 H, m), 7.00 (2 H, m), 7.1–7.3 (3 H, m), 7.69 (1 H, t, J = 7.4 Hz), 7.7–7.8 (2 H, m), 8.17 (1 H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 63.5, 74.5, 85.2, 116.0, 128.0, 128.1, 128.2, 128.4, 128.5, 132.7, 133.1, 134.8, 134.9, 140.0, 143.2, 185.5, 187.4. Anal. Found: C, 66.49; H, 3.52; Cl, 20.37. Calcd for $C_{19}H_{12}O_2Cl_2$: C, 66.49; H, 3.52; Cl, 20.66.

The diastereomer mixture of **4b**, **4b′** (4:1) was separated by flash column chromatography (hexane–ether–2-propanol, 200:5:0.5). The former band contains **4b′** and the latter one contains **4b**.

1,6-Dichloro-7-methylene-8-(4-methylphenyl)benzo[3,4]-bicyclo[4.2.0]oct-3-ene-2,5-dione. Major isomer (4b): white crystals from methanol; mp 116–119 °C; MS *m*/*e* 356, 358, 360 (M$^+$); IR (KBr) 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.36 (3 H, s), 4.70 (1 H, m), 5.47 (1 H, m), 5.95 (1 H, m), 7.18 (2 H, s), 7.34 (2 H, s), 7.88 (2 H, m), 8.24 (2 H, m). Anal. Found: C, 66.94; H, 3.84; Cl, 19.94. Calcd for $C_{20}H_{14}O_2Cl_2$: C, 67.24; H, 3.95; Cl, 19.85.

Minor isomer (4b′): pale red crystals from chloroform–methanol; mp 138–141 °C; MS *m*/*e* 356, 358, 360 (M$^+$); IR (KBr) 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.26 (3 H, s), 5.11 (1 H, m), 5.37 (1 H, m), 5.65 (1 H, m), 6.86 (2 H, d, J = 7.9 Hz), 6.99 (2 H, d, J = 7.9 Hz), 7.69 (1 H, t, J = 7.7 Hz), 7.7–7.9 (2 H, m), 8.16 (1 H, d, J = 7.6 Hz). Anal. Found: C, 67.00; H, 3.89; Cl, 20.10. Calcd for $C_{20}H_{14}O_2Cl_2$: C, 67.24; H, 3.95; Cl, 19.85.

7,8-Dichloro-2,3-dihydro-2-(diphenylmethylidene)-6-hydroxy-3-methylbenzo[*de*]chromene (6): white crystals from hexane–chloroform; mp 187–189 °C; MS *m*/*e* 432, 434, 436 (M$^+$); IR (KBr) 3500 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.89 (3 H, d, J = 6.7 Hz), 4.65 (1 H, q, J = 6.7 Hz)8 5.76 (1 H, br s), 7.0–7.3 (11 H, m), 7.47 (1 H, t, J = 7.3 Hz), 8.09 (1 H, d, J = 8.5 Hz); ^{13}C

NMR ($CDCl_3$) δ 10.4 (q), 58.8 (d), 110.8 (s), 112.5 (s), 113.5 (s), 119.4 (s), 121.0 (d), 122.0 (s), 126.0 (d), 126.9 (d), 127.1 (d), 127.8 (d), 130.0 (d), 136.8 (s), 141.5 (s), 142.0 (s), 142.6 (s), 151.7 (s). Anal. Found: C, 72.32; H, 4.02; Cl, 16.17. Calcd for $C_{26}H_{18}O_2Cl_2$: C, 72.07; H, 4.19; Cl, 16.36.

Photochemical Reaction of 1a with 1,1-Diphenyl-d_{10}-3-methylallene. A benzene solution containing **1a** (1 mmol) and **2l′** (2 mmol) was irradiated for 9 h in a similar manner. After separation by flash column chromatography **6** was obtained in 39% yield: MS *m/e* 442, 444, 446 (M^+); ^1H NMR ($CDCl_3$) δ 1.89 (3 H, d, J = 6.7 Hz), 4.65 (1 H, q, J = 6.7 Hz), 5.76 (1 H, br s), 7.04 (1 H, d, J = 7.3 Hz), 7.47 (1 H, t, J = 7.3 Hz), 8.09 (1 H, d, J = 8.5 Hz).

Ozonolysis of 6. A solution of **6** (80 mg, 0.19 mmol) in 40 mL of MeOH–CH_2Cl_2 (1:1) was subjected to ozonolysis. The crude product mixture was concentrated in vacuo, giving a residue which was subjected to column chromatography to give polymerized products and benzophenone (5 mg, 15%).

Examination of the Initial Stage of the Photochemical Reaction of 1a with 1,1-Diphenylallenes. Irradiation (366 nm[50] or >340 nm (through a Toshiba UV-36 glass filter)) of a argon-bubbled solution (3 mL) of 2,3-dichloro-1,4-naphthoquinone (0.01 M) and 1,1-diphenylallenes (0.02 M) with a high-pressure Hg lamp in a appropriate solvent was done in a UV cell for a given time. No change in light intensity was detected during these experiments. The reaction mixture was concentrated in vacuo and dissolved in a 600 μL of $CDCl_3$ containing an internal standard. The relative amount of spiropyran adduct **3** for an internal standard was determined by integral by using 400-MHz ^1H NMR spectroscopy. Total conversion did not exceed 10%.

CIDNP Examination. A typical CIDNP examination of the photochemical reaction is as follow: suitable amounts ($\sim 10^{-2}$ M) of **1** and **2** were dissolved in an acetonitrile-d_3 or benzene-d_6 in a Pyrex NMR sample tube. The sample was irradiated at room temperature under argon by a high-pressure Hg lamp through a glass filter (Toshiba UV-37), and the ^1H NMR signals were observed before, during, and after irradiation by a JEOL PS-100 spectrometer.

Reduction Potential Measurements. The reduction potential of quinones and oxidation potential of allenes were obtained by a PAR Model 174 cyclic voltammetry. The working electrode was platinum wire. A Ag/Ag^+ (0.1 M) electrode was used as a reference and 0.1 M tetraethylammonium perchlorate as supporting electrolyte. The reduction potential of **1** measured in a nitrogen-purged acetonitrile solution showed nice reversibility, while the oxidation potential of **2** did not.

Crystal Structure for 3g. The structure analyses were made with a Rigaku Denki AFC-4 automatic four-circle diffractometer [Ni-filtered Cu Kα radiation (1.541 84 Å), ω–2θ scan technique, 2θ ≤ 120°, scan speed 4° min^{-1} (θ), scan range (1.5 + 0.15 tan θ)°]. Three standard reflections measured every 100 reflections showed no significant X-ray damage or crystal decay. A total of 6591 unique (for **3g**) reflections were used for structure determination. The structure was solved by direct methods with MULTAN 78[51] (with atomic scattering factors from *International Tables for X-ray Crystallography*)[52] and refined by block-diagonal least-squares[53] methods with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. **3g**: $R = 0.0721$ and $R_2 = 0.0703$, where $\omega = 1.0$ for $F_{obsd} \neq 0$, $\omega = 0.8$ for $F_{obsd} = 0.0$.

Crystal data are as follows: (**3g**) $a = 15.877$ (1), $b = 14.615$ (1), and $c = 10.256$ (1) Å; $\alpha = 78.96$ (1); $\beta = 74.26$ (1); $\gamma = 89.79$ (1)°; space group = $P1$ (triclinic) ($Z = 4$); $V = 2245$ (1) $Å^3$, D_c/g cm^{-3} = 1.324.

Acknowledgment. We are grateful to Professor Nobuo Tanaka at Tokyo Institute of Technology and Professor Yukiteru Katsube and Dr. Mamoru Sato at Institute for Protein Research, Osaka University, for the measurement of X-ray analysis. We also thank Professor Tadamasa Shida at Kyoto University for his helpful discussion.

Supplementary Material Available: 2D COSY ^1H NMR spectra of **3f** and **6**, 2D COSY ^{13}C–^1H NMR spectrum of **4a**, atomic positional and equivalent isotropic thermal parameters for **3g**, and bond distances and angles of **3g** (7 pages). Ordering information is given on any current masthead page.

---

(50) Parker, C. A. *Proc. R. Soc. London Ser. A* **1952**, *220*, 104. Hatchard, D. A.; Parker, C. A. *Proc. R. Soc. London Ser. A* **1956**, *235*, 518.

(51) Main, P.; Fall, S. E.; Lessingen, L.; Genmain, G.; Delclercq, J. P.; Woolfson, M. M. In a System of Computer Programs for the Automatic Solution of Crystal Structure from X-ray Diffraction Data; MULTAN 78. University of York; 1978.

(52) In *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kyroch Press: Birmingham, 1974; Vol. 4.

(53) Ashida, T. HBLS 5 in the Universal Crystallographic Computing System Osaka; The Computation Center, Osaka University; 1979, 531.