# The Photochemical Reaction of 2-Alkoxy-1,4-naphthoquinones with Olefins. III.[1] The Re-examination of the Structures of the Photo-addition Compounds and the Reaction Mechanism

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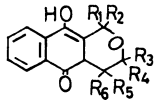
In the photochemical reaction of 2-alkoxy-1,4-naphthoquinones with a variety of olefins, two types of photo-addition compounds are found to be produced: the cyclobutane-ring compounds and the oxetanol-ring compounds. Although the present author has assigned the structure of a tetrahydropyran-ring compound to one of the photo-addition compounds primarily on the basis of the analyses of the spectral data, the previously proposed structures should be corrected to an oxetanol-ring compound on the basis of the chemical reactivities. Although some cyclobutane-ring compounds were stable enough to be isolated as final reaction products, the other cyclobutane-ring compounds, though once produced, were too unstable to undergo the subsequent photochemical reaction to give oxetanol-ring compounds on further irradiation. The stability of the cyclobutane-ring compounds was dependent on both the substituents of the olefins and the wavelength of the light. The origin of the stability and the reaction mechanism were investigated.

A variety of compounds characterized by their stimulating physiological activity have been synthesized by means of the photochemistry of quinones.[2] Thus, the photochemical reactions of quinones with olefins have attracted several workers.[3-8] Although 1,4-naphthoquinone has been known to yield photo-addition compounds with olefins, the yields are, in general, low, partly because the photo-reduction of 1,4-naphthoquinone proceeds competitively to form such photo-reduction compounds as 1,4-naphthoquinhydrones or 1,4-naphthalenediol. These complicated features originate partly from the higher oxidation potential of 1,4-naphthoquinone.[9,10]

2-Alkoxy-1,4-naphthoquinones, on the other hand, have lower oxidation potentials than that of 1,4-naphthoquinone;[9,10] hence, the photo-addition products of 2-alkoxy-1,4-naphthoquinones with olefins could be isolated in fairly good yields as a result of a smooth reaction, while there were no photo-reduction products such as quinhydrones or 1,4-diol. The photo-addition compounds obtained in the reaction mentioned above could be classified into two types. Although the present author has assigned the structure of 10-hydroxy-3,4,4a,5-tetrahydro-1*H*-naphtho[2,3-*c*]pyran-5-one derivatives, **1**, to one of the photo-addition compounds[1] primarily on the basis of the analyses of the spectral data, every attempt to derive **1** to 1,4-naphthoquinone derivatives or 1,4-naphthalenediol derivatives *via* keto-enol change, has proven unsuccessful. Thus, in this report the previously proposed structure, **1**, will be revised to the structure, **2**, that of the oxetanol derivatives. The chemical evidences preferring the structure **2** to **1** will be presented. In addition, the course of the reaction was much influenced by both the substituents of the olefins and the wavelength of the light. The mechanism of the reaction, as well as the factors determining these photo-addition products, was investigated.



**1**

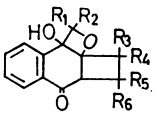
## Results and Discussion

The 2-alkoxy-1,4-naphthoquinones examined here are 2-methoxy-, 2-ethoxy-, 2-isopropoxy-, and 2-allyloxy-1,4-naphthoquinones. The olefins selected in this work are 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, cyclohexene, cyclooctene, 1,5-cyclooctadiene, 2-bicyclo[2.2.1]heptene, 2,5-bicyclo[2.2.1]heptadiene, styrene, indene, α-methylstyrene, 1,1-diphenylethylene, and 1,1-di-*p*-tolylethylene.

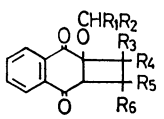
A benzene solution of a mixture of a 2-alkoxy-1,4-naphthoquinone and an olefin was subjected to irradiation by a high-pressure Hg arc lamp with and/or without the application of a filter, A or B. The transmission characteristics of the filters, A and B, are shown in Table 1. Neither the precipitation of 2-alkoxy-1,4-naphthoquinhydrones nor any coloration was observed during the course of the reaction, even when olefin had active hydrogen atoms, such as 1-hexene; that is, the reaction proceeded smoothly. This is one of the extremely different features of 2-alkoxy-1,4-naphthoquinones compared with 1,4-naphthoquinone itself. The structures of these photo-addition compounds, which were obtained in fairly good yields in every case examined here, proved to be classifiable into two types, **2** and **3**, depending on both the substituents of the olefins and the wavelength of the light.

Table 1. Transmission characteristics of the filter

| | 0% Transmission (nm) | 50% Transmission (nm) | 90% Transmission (nm) |
|---|---|---|---|
| Filter A | 360 | 390 | 450 |
| Filter B | 390 | 420 | 470 |



( or the structure 1 )

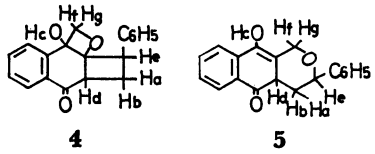


**2** **3**

When 2-alkoxy-1,4-naphthoquinones and olefins, with the exceptions of 1,1-diphenylethylene and 1,1-di-

*p*-tolylethylene, were subjected to photochemical reactions under irradiation with no filter, the photo-addition products proved to have, in general, the structure, **2**. On irradiation with use of a filter (A or B), however, these olefins yielded another type of photo-addition compound, **3**. Under the conditions with and/or without a filter, on the other hand, 1,1-diphenylethylene or 1,1-di-*p*-tolylethylene was found to give exclusively the photo-addition compound, **3**. First, the determination of the structures of the photo-addition products will be described.

*The Re-examination of the Structure of the Photo-addition Compounds, 2*: The re-examination of the structure of the photo-addition compounds, **2**, will be illustrated by referring to the photo-product obtained in the reaction of 2-methoxy-1,4-naphthoquinone with styrene, a typical example. A benzene solution (20 ml) of 2-methoxy-1,4-naphthoquinone (1 mmol) and styrene (2 mmol) was subjected to irradiation by a high-pressure Hg arc lamp (300 W) without a filter until the quinone was completely consumed. The quantum efficiency of the photochemical reaction for the disappearance of 2-methoxy-1,4-naphthoquinone in its reaction with styrene was estimated to be 0.18 (with the filter, A). After the usual work-up of the reaction mixture, white needles were obtained as the main reaction product in a 69% yield. The elemental analysis and the molecular weight determined by mass spectrometry reveal that the photo-addition compound was composed of one molecule of 2-methoxy-1,4-naphthoquinone and one molecule of styrene. The photo-addition compound contained both a hydroxyl group and a carbonyl group, judging from the inspection of the IR and UV spectra. In the $^1$H-NMR spectrum (Fig. 1), the signal corresponding to $H_c$ disappeared after the treatment of the chloroform solution with $D_2O$. The nuclear spin-spin interactions among $H_a$, $H_b$, $H_d$, and $H_e$ were confirmed by the spin decoupling technique. When 2-methoxy-$d_3$-1,4-naphthoquinone was subjected to the same photochemical reaction, the $^1$H-NMR signals corresponding to $H_f$ and $H_g$ (Fig. 1) disappeared. On the other hand, the $^1$H-NMR signal corresponding to $H_d$ disappeared completely when 2-methoxy-1,4-naphthoquinone-3-*d* was used in the reaction. These results indicate that the protons, denoted by $H_d$, $H_f$, and $H_g$, of the photo-addition compound originated from the 2-methoxy-1,4-naphthoquinone moiety. Taking into consideration either of the two structures, **4** or **5**, one can reasonably explain the spectral data of the photo-addition compound. Of these, **4** was characterized by an oxetanol ring as well as a cyclobutane ring. A similar structure was once suggested by Anett[11] for the reaction product obtained by the photochemical reaction of 2-methoxy-1,4-naphthoquinone with vinyl acetate and by Ellis and Jones[12] for the photo-dimerization product of 2-methoxy-1,4-naphthoquinone. On the other hand, **5**, characterized by a tetrahydropyran ring and previously proposed by the present author,[1] should be converted to 1,4-naphthoquinone derivatives or 1,4-naphthalenediol derivatives *via* a keto-enol change. Every attempt to do so, how-



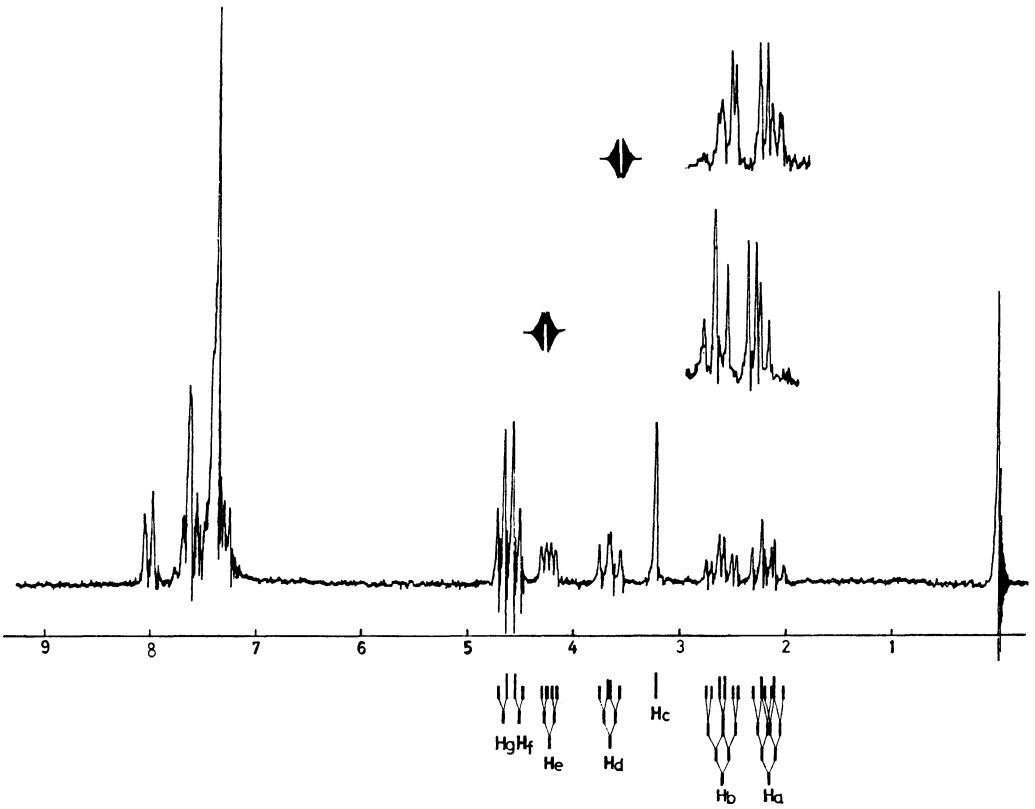
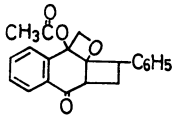



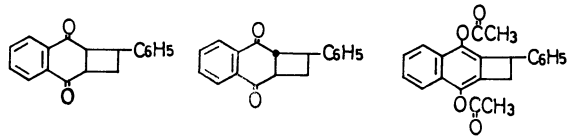

Fig. 1. $^1$H-NMR spectrum of the photo-addition compound.

ever, had no success. When the photo-addition compound was acetylated with acetic anhydride for 3 h, a mono-acetylated product, **6**, was obtained (yield: 83%).[13]



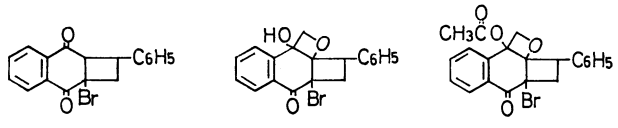
**6**

*The Acid-catalyzed Decomposition of the Photo-addition Compound*: After the treatment of the photo-addition compound with hydrochloric acid or sulfuric acid in a chloroform solution at room temperature, a mixture of two products, **7a** and **7b**, was isolated in a 60% yield. **7a** and **7b** have the same molecular weight, suggesting that a formaldehyde unit is released during the treatment. By the photochemical reaction of 1,4-naphthoquinone with styrene we obtained, in actual, the same mixture of **7a** and **7b**, although the relative ratio of the two compounds was not compatible. The 1,4-diacetoxynaphthalene derivative, **8**, was isolated as the sole reaction product when **7a**, as well as **7b**, was treated by sodium acetate–acetic anhydride under reflux conditions. These results confirmed that **7a** and **7b** are isomeric with each other.[14]



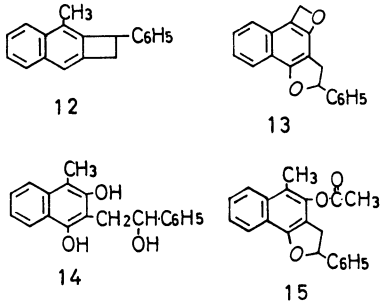
**7a** **7b** **8**

*The Bromination of the Photo-addition Compound*: The bromination of the photo-addition compound with bromine in a chloroform solution at room temperature gave a mixture of two compounds, **9** (54%) and **10** (32%). Since **10** was revealed to have a hydroxyl group through the inspection of the IR spectrum, the acetylation of **10** was performed and an acetyl derivative, **11**, was isolated. **9** and **11** were also obtained through the bromination of the acetyl derivative of the photo-addition compound, **6**, in 50 and 36% yields respectively. The structure of **9** was further confirmed by the isolation of **9** as one of the reaction products from the bromination reaction of **7b**.



**9** **10** **11**

*The Clemmensen Reduction of the Photo-addition Compound*: Three reaction products, **12**, **13**, and **14**, were isolated from the reaction mixture of the Clemmensen reduction of the photo-addition compound in 17, 7, and 12% yields respectively. **12** was revealed to be the derivative of 1-methylnaphthalene through the isolation of 1-methylnaphthalene as the thermal decomposition product of **12**. The coloration of **14** to deep yellow by ferric sulfate in ethanol suggested the existence of the phenolic hydroxyl group; this is confirmed by the fact that the acetylation of **14** with sodium acetate–acetic anhydride yielded an acetyl derivative, **15**. Moreover, the possibility of 1,4-naphthalenediol derivatives could be excluded since the oxidation of **14** by silver oxide in ether failed to yield 1,4-naphthoquinone derivatives.



12 13

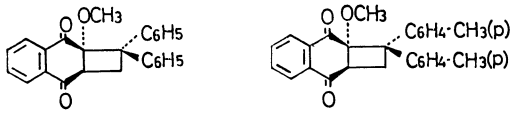
14 15

*The $^{13}C$-NMR Spectrum of the Photo-addition Compound*: The $^{13}C$-NMR spectrum of the photo-addition compound was measured in a solution of chloroform (the chemical shifts were calibrated from TMS as the internal standard): $\delta$; 26.63, 43.44, 49.63, 70.62, 82.33, 90.95, 126.92, 127.05, 127.41, 128.26, 129.17, 130.26, 134.93, 137.60, 143.43, and 197.24 ppm. These data suggest that the photo-addition compound contains six different kinds of $sp^3$-carbon atoms as its constituents.

From the results described above, it can be deduced that the photo-addition compound should have the structure, **4**, characterized by an oxetanol ring as well as a cyclobutane ring. Here, the present author would like to correct the previously proposed structure, **5**, for the photo-addition compound.

A similar type of photo-addition compound, **2**, obtained in the photochemical reaction of 2-alkoxy-1,4-naphthoquinone with olefins is tabulated in Table 2.

*The Structure of the Photo-addition Compounds*, **3**: As a typical example, the photochemical reaction of 2-methoxy-1,4-naphthoquinone with 1,1-diphenylethylene will be described. A benzene solution (20 ml) of 2-methoxy-1,4-naphthoquinone (1 mmol) and 1,1-diphenylethylene (2 mmol) was subjected to irradiation by high-pressure Hg arc lamp (300 W) without a filter. After the complete consumption of the quinone, white crystals were isolated as a sole reaction product in a 63% yield. The elemental analysis and the mass data require that the photo-addition compound is composed of one molecule each of 2-methoxy-1,4-naphthoquinone and 1,1-diphenylethylene. The IR and UV spectra show the existence of the carbonyl group, but not the hydroxyl group. The $^1H$-NMR spectrum was compatible with the structure, **3a**. The assignment of the $^1H$-NMR signals was concreted by the reaction using 2-methoxy-$d_3$-1,4-naphthoquinone as the starting material. Upon being heated in carbon tetrachloride, the photo-addition compound, **3a**, decomposed again to give 2-methoxy-1,4-naphthoquinone and 1,1-diphenylethylene quantitatively. The half-life of **3a** was estimated to be about 92 min at 75±1 °C.

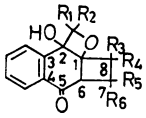


**3a** **3b**

Table 2. The photo-addition compounds obtained in the reaction of 2-alkoxy-1,4-naphthoquinones with olefins

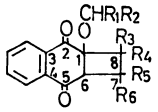
| 2-Alkoxy-1,4-naphthoquinone | Olefin | Yields of the Photo-addition Compounds[a] | |
|---|---|---|---|
| | | **2** | **3** |
| 2-Methoxy-1,4-naphthoquinone | 1-Hexene | 25% (**2a**) | |
| 2-Methoxy-1,4-naphthoquinone | 1-Heptene | 50 (**2b**) | |
| 2-Methoxy-1,4-naphthoquinone | 1-Octene | 67 (**2c**) | 40%[b] (**3e**) |
| 2-Methoxy-1,4-naphthoquinone | 1-Nonene | 48 (**2d**) | |
| 2-Methoxy-1,4-naphthoquinone | 1-Decene | 45 (**2e**) | |
| 2-Methoxy-1,4-naphthoquinone | Cyclohexene | 39 (**2f**) | |
| 2-Methoxy-1,4-naphthoquinone | Cyclooctene | 74 (**2g**) | |
| 2-Methoxy-1,4-naphthoquinone | 1,5-Cyclooctadiene | 29 (**2h**) | |
| 2-Methoxy-1,4-naphthoquinone | 2-Bicyclo[2.2.1]heptene | 50 (**2i**) | |
| 2-Methoxy-1,4-naphthoquinone | 2,5-Bicyclo[2.2.1]heptadiene | 35 (**2j**) | |
| 2-Methoxy-1,4-naphthoquinone | Indene | 73 (**2k**) | |
| 2-Methoxy-1,4-naphthoquinone | Styrene | 69 (**2l**=**4**) | 50[c] (**3d**) |
| 2-Methoxy-1,4-naphthoquinone | α-Methylstyrene | 9 (**2m**) | 69[d] (**3c**) |
| 2-Methoxy-1,4-naphthoquinone | 1,1-Diphenylethylene | | 63 (**3a**) |
| 2-Methoxy-1,4-naphthoquinone | 1,1-Di-*p*-tolylethylene | | 71 (**3b**) |
| 2-Ethoxy-1,4-naphthoquinone | Styrene | 60 (**2n**) | |
| 2-Ethoxy-1,4-naphthoquinone | 1,1-Diphenylethylene | | 60 (**3f**) |
| 2-Isopropoxy-1,4-naphthoquinone | Styrene | 7.1 (**2o**) | 41 (**3g**)[e] |
| 2-Allyloxy-1,4-naphthoquinone | Styrene | 27 (**2p**) | |

a) The yields were calculated on the basis of the quinones consumed in the photochemical reaction without a filter, unless otherwise mentioned. b) The yield was calculated after 90% of the quinone has been consumed in the photochemical reaction with the filter A. c) The yield was calculated after 89% of the quinone has been consumed in the photochemical reaction with the filter A. d) The yield was calculated for a mixture of two isomers, **3c**-I and **3c**-II. e) In a previous report, 2,2-dimethyl-3-phenyl-3,4,4a,-5,10,10a-hexahydro-2*H*-naphtho[2,3-*b*]pyran-5,10-dione was suggested as the probable structure of **3g**. However, **3g** was deduced to have a cyclobutane ring because the IR and UV spectra of **3g** have characteristics similar to those of **3d**, and as the product of ether cleavage of **3g** we obtained 1-hydroxy-8-phenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione; IR(liq. film); 3400(OH), 1670 $cm^{-1}$ (C=O). $^1$H-NMR($CDCl_3$); $\delta$: 2.30—3.00(2H, C-7 $CH_2$, m), 2.80 (1H, OH, s), 3.38 (1H, C-6 CH, dd, $J$=4.0, 8.0 Hz), 3.92 (1H, C-8 CH, dd, $J$=2.0, 8.0 Hz), 7.10—8.20 ppm (9H, aromatic-H, m).



**2**

| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ |
|---|---|---|---|---|---|---|
| **2a** | H | H | $C_4H_9$(*n*) | H | H | H |
| **2b** | H | H | $C_5H_{11}$(*n*) | H | H | H |
| **2c** | H | H | $C_6H_{13}$(*n*) | H | H | H |
| **2d** | H | H | $C_7H_{15}$(*n*) | H | H | H |
| **2e** | H | H | $C_8H_{17}$(*n*) | H | H | H |
| **2f** | H | H | H | $-(CH_2)_4-$ | | H |
| **2g** | H | H | H | $-(CH_2)_6-$ | | H |
| **2h** | H | H | H | $-(CH_2)_2$ $(CH_2)_2-$ (CH=CH) | | H |
| **2i** | H | H | H | $-CH-CH_2-CH-$ $(CH_2)_2$ | | H |
| **2j** | H | H | H | $-CH-CH_2-CH-$ CH=CH | | H |
| **2k** | H | H | H | $-C_6H_4CH_2$(*o*)$-$ | | H |
| **2l** | H | H | $C_6H_5$ | H | H | H |
| **2m** | H | H | $C_6H_5$ | $CH_3$ | H | H |
| **2n** | $CH_3$ | H | $C_6H_5$ | H | H | H |
| **2o** | $CH_3$ | $CH_3$ | $C_6H_5$ | H | H | H |
| **2p** | $CH=CH_2$ | H | $C_6H_5$ | H | H | H |



**3**

| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | $R_6$ |
|---|---|---|---|---|---|---|
| **3a** | H | H | $C_6H_5$ | $C_6H_5$ | H | H |
| **3b** | H | H | $C_6H_4\cdot CH_3$(*p*) | $C_6H_4\cdot CH_3$(*p*) | H | H |
| **3c** | H | H | $C_6H_5$ | $CH_3$ | H | H |
| **3d** | H | H | $C_6H_5$ | H | H | H |
| **3e** | H | H | $C_6H_{13}$(*n*) | H | H | H |
| **3f** | $CH_3$ | H | $C_6H_5$ | $C_6H_5$ | H | H |
| **3g** | $CH_3$ | $CH_3$ | $C_6H_5$ | H | H | H |

*The Structure of the Photo-addition Compounds and Its Relation to the Substituents of Olefins and the Wavelength of Irradiation*: With 1,1-diphenylethylene or 1,1-di-*p*-tolylethylene, 2-alkoxy-1,4-naphthoquinone was found to yield exclusively the photo-addition compound, **3a** or **3b**, characterized by a cyclobutane ring, independent of the wavelength of irradiation. On the other hand, in the photochemical reaction of 2-alkoxy-1,4-naphthoquinone with olefins other than 1,1-diphenylethylene and 1,1-di-*p*-tolylethylene, both of the two different types of photo-addition compounds, **2** and **3**, were obtained, depending on whether the irradiation was with or without a filter (Table 2).

In the photochemical reaction of the quinone with α-methylstyrene, the photo-addition compound, **3c**, was the main reaction product (69% yield); the photo-addition compound, **2m**, was obtained as a minor reaction product (9% yield) on irradiation without a filter. In contrast with the case of α-methylstyrene without a filter, the photo-addition compound, **2l** or **2c**, characterized by an oxetanol ring as well as a cyclobutane ring, could be isolated as a stable product in the reaction of the quinone with another olefin, such as styrene or 1-octene, but none of any cyclobutane-ring compound, such as **3d** or **3e**, could be obtained after the consumption of the quinone had been completed (Fig. 2). By cutting the light of a shorter wavelength with a filter (A or B), one could obtain, however, a cyclobutane-ring compound, **3d** or **3e**, as well as an oxetanol-ring compound, **2l** or **2c**, even in a reaction with styrene or with 1-octene (Fig. 3). The results obtained above indicate that the cyclobutane-ring compounds, once produced, undergo further reaction upon irradiation at a shorter wavelength to the oxetanol-ring compounds, depending on their stabilities. Thus, the tendency of the susceptibility to further reactions is as follows: adduct from 1,1-diphenylethylene or its derivatives < adduct from α-methylstyrene < adduct from the other olefins, such as styrene or 1-octene. The source of the stability of the adduct, **3**, to the light will be discussed in the following sections.

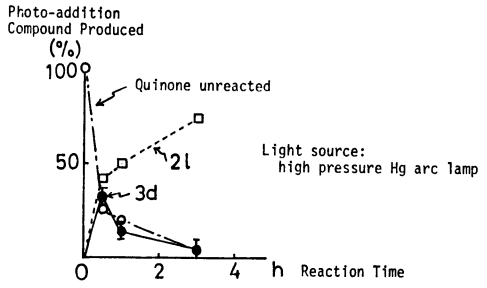



Fig. 2. Photochemical reaction of 2-methoxy-1,4-naphthoquinone with styrene.

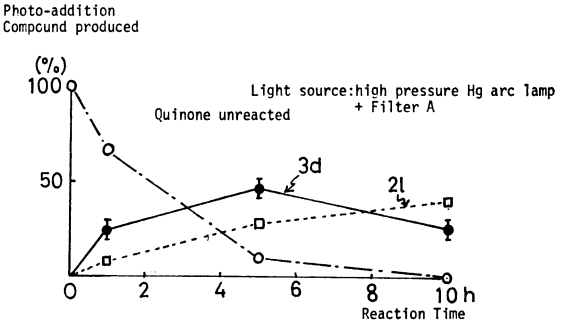



Fig. 3. Photochemical reaction of 2-methoxy-1,4-naphthoquinone with styrene.

*The Stability of the Photo-addition Compounds, 3, in Relation to the Substituents of Olefins*: The absorption characteristics of the photo-addition compounds, **3**, are summarized in Table 3. In the UV spectrum of **3a** dissolved in carbon tetrachloride or acetonitrile, a new shoulder at a longer wavelength [365 nm($CCl_4$), 361 nm($CH_3CN$)] appeared which could not be observed in **3d** or **3e**. This absorption can be compared in its wavelength and absorption coefficient [$UV_{max}$ ($CH_3CN$): 340 nm ($\varepsilon$: 597)] to the charge-transfer band observed in [2,2]paracyclophanequinone.[15] This suggests that the intramolecular interactions exist in the photo-addition compound, **3a**.

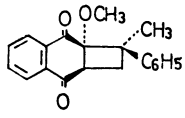
Table 3. The absorption characteristics of the photo-addition compounds **3**

| Photo-addition compounds | Solvents | Absorption characteristics nm ($\varepsilon$) |
|---|---|---|
| **3a** | $CCl_4$ | 303($2.0\times10^3$), 312($1.9\times10^3$), 352($1.7\times10^2$), 365($1.5\times10^2$) |
| | $CH_3CN$ | 303($1.9\times10^3$), 312($1.7\times10^3$), 349($1.5\times10^2$), 361($1.4\times10^2$) |
| **3d** | $CCl_4$ | 301($2.8\times10^3$), 310($2.6\times10^3$), 343($4.5\times10^2$) |
| | $CH_3CN$ | 301($2.6\times10^3$), 301($2.4\times10^3$), 339($4.5\times10^2$) |
| **3e** | $CCl_4$ | 300($1.4\times10^3$), 309($1.3\times10^3$), 352($1.6\times10^2$) |
| | $CH_3CN$ | 300($1.5\times10^3$), 308($1.4\times10^3$), 349($1.7\times10^2$) |

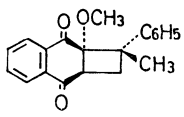
These intramolecular interactions could be understood further by an inspection of the $^1$H-NMR data. That is, the ring protons of phenyl groups in the compound, **3a**, show complicated $^1$H-NMR signals which otherwise show broad singlet-like $^1$H-NMR signals such as those in 1,1-diphenylethylene as a starting olefin. The intramolecular interactions are demonstrated more clearly by the $^1$H-NMR spectrum of **3b** in carbon tetrachloride, which exhibits the existence of two different kinds of *p*-tolyl groups. That is, two different kinds of methyl protons appeared at $\delta$=2.06 and 2.28 ppm, and two different sets of a multiplet of four protons appeared as an AB-quartet pattern which is characteristic of a para-substituted benzene ring. One of these AB-quartets possessed $\delta$-values of 6.75 and 7.01 ppm ($J$=10.0 Hz), and the other, those of 7.01 and 7.27 ppm ($J$=8.0 Hz). The methyl protons of 1,1-di-*p*-tolylethylene as a starting olefin, on the other hand, appeared at $\delta$=2.36 ppm and an AB-quartet of the aromatic protons possesses $\delta$-values of 7.01 and 7.15 ppm ($J$=8.0 Hz). A comparison of these $^1$H-NMR data with those of the starting olefins shows that the chemical shifts of the protons belonging to one of the *p*-tolyl groups move to higher field in the photo-addition compound, **3b**. Presumably these shifts to a higher field originate from the anisotropy of the aromatic rings as well as the carbonyl

groups of the quinone moiety in the compound, **3b**. In fact, an inspection of the molecular model reveals that the quinone moiety and one of the *p*-tolyl groups of the olefin moiety are in close proximity.

These results presented above suggest the existence of intramolecular interactions through $\pi$-electrons in the cyclobutane type of the photo-addition compounds, **3**, derived from 2-methoxy-1,4-naphthoquinone and 1,1-diphenylethylene or its derivatives.




**3c-I**




**3c-II**

In the photochemical reaction of 2-methoxy-1,4-naphthoquinone with $\alpha$-methylstyrene, the adduct obtained was confirmed to be a mixture of **3c**-I and **3c**-II from an inspection of the $^1$H-NMR spectra. Because of the non-symmetrical nature of $\alpha$-methylstyrene, the possible formation of two isomers is explicable; *i.e.*, one is an isomer which has intramolecular interactions between the quinone moiety and the phenyl group of the olefin moiety through $\pi$-electrons, **3c**-I, while the other is an isomer which has no interactions, **3c**-II. On irradiation by a high-pressure Hg arc lamp without a filter, the ratio of the isomer contents, **3c**-I/II, was estimated to be 1.0/1.5, as determined by the integration of the $^1$H-NMR signals. The ratio, **3c**-I/II, was found to be dependent on the wavelength of the light source used (Table 4). The relative ratio of the isomers, **3c**-I/II, is

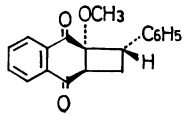
Table 4. The ratio of the isomer contents, **3c**-I/II, in the photochemical reaction of 2-methoxy-1,4-naphthoquinone with $\alpha$-methylstyrene[a)]

| Filter used[b)] | **3c**-I | **3c**-II |
|---|---|---|
| None | 1.0 | 1.5 |
| Filter A | 1.0 | 3.9 |
| Filter B | 1.0 | 5.1 |

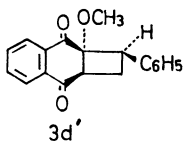
a) The ratio was estimated on the basis of the integration of the $^1$H-NMR signals of the mixture. b) The light source used was a high-pressure Hg arc lamp.

increased as the relative transmittance at the shorter wavelength is increased by changing the filters. Moreover, on irradiating a benzene solution of a mixture of the two isomers in a Pyrex glass tube by means of a high-pressure Hg arc lamp without a filter, **3c**-II was found to decompose selectively. These results indicate that the isomer, **3c**-I, is more stable than **3c**-II. That is, the cyclobutane ring in the photo-addition compound, **3**, is deduced to be stabilized by intramolecular interactions through $\pi$-electrons. The energy relaxation mode *via* the intramolecular interactions might play a considerably important role in the photo-addition compound, **3**, although the sterical requirements exerted by the substitutents of the olefin moiety should also be taken into consideration at the same time for the H-abstraction by excited carbonyl groups in **3**.[16)]

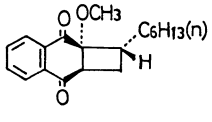
From the results tabulated in Table 4 one can observe that the amount of the isomer, **3c**-II, always surpassed that of **3c**-I. The formation of **3c**-I is less favored, presumably because of the sterical requirements, though the isomer, **3c**-I, once formed, may be more stable than **3c**-II on further irradiation. These sterical requirements might play a more important role in the selective formation of a cyclobutane-ring compound in the case of styrene or 1-octene than in $\alpha$-methylstyrene. Only one of the possible isomers, **3d** or **3e**, could be obtained, but neither **3d'** nor **3e'**, when styrene or 1-octene and 2-methoxy-1,4-naphthoquinone were submitted to irradiation with a filter. The cyclobutane-ring compound, **3d** or **3e**, was confirmed to have no intramolecular interactions by an inspection of the UV and $^1$H-NMR spectra.



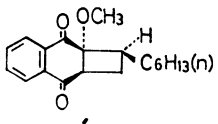

3d




3d'

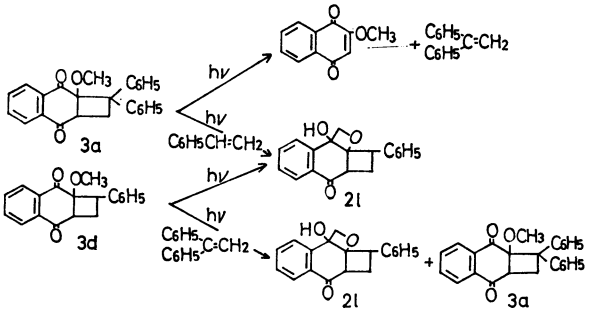



3e




3e'

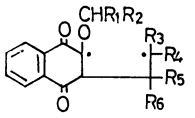
*The Reversibility of the Formation of the Cyclobutane-ring Compounds, 3*: On further irradiation without a filter, the cyclobutane-ring compound, **3a**, slowly photo-decomposed to give 2-methoxy-1,4-naphthoquinone and 1,1-diphenylethylene. Moreover, when, under the same conditions, the photochemical decomposition of the compound, **3a**, was investigated in the presence of an excess of styrene, the sole reaction product isolated was determined to be **21**; the same product as that derived from the photochemical reaction of 2-methoxy-1,4-naphthoquinone with styrene without a filter. On the other hand, since the cyclobutane-ring compound, **3d**, quantitatively photo-rearranged to the compound, **21**,[17)] a similar photochemical reaction of **3d** was examined in the presence of an excess of 1,1-diphenylethylene; then the compound, **3a**, was isolated as well as **21**. These results are illustrated in Scheme 1. The results presented can all be explained assuming that the formation of a cyclobutane-ring compound is reversible on irradiation.




Scheme 1.

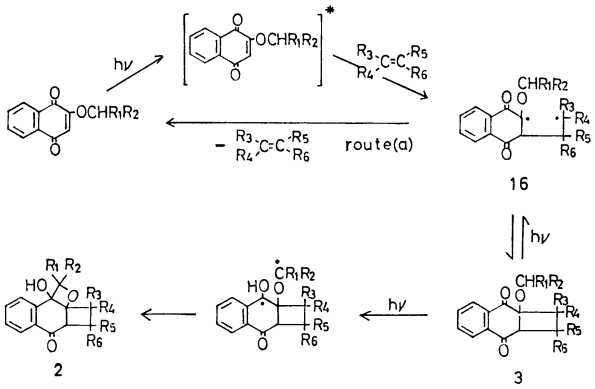
*The Reaction Scheme.* In the photochemical reaction of 2-alkoxy-1,4-naphthoquinones with olefins, the first stage of the reaction should be the formation of cyclobutane-ring compounds, **3**, from the photo-excited

quinones and olefins. Severals of the cyclobutane-ring compounds derived from such olefins as 1,1-diphenylethylene, 1,1-di-*p*-tolylethylene and α-methylstyrene are stabilized by intramolecular interactions through π-electrons as well as by sterical requirements for the intramolecular H-abstraction by an excited carbonyl group.[16] In another case, the cyclobutane-ring compounds are rather unstable upon further irradiation to undergo the subsequent photochemical reaction *via* intramolecular H-abstraction by a carbonyl group to yield the oxetanol-ring compounds, **2**, which are themselves stable upon further irradiation. The extent of the reversible reaction to the starting quinone and the olefin (Route (a)) is considerable for the diradical, **16**, derived from **3a**, **3b**, **3c**, or **3f**, presumably because of the lower dissociation energy of the bond connecting the quinone with olefin moieties. The bonding between the quinone and olefin moieties of the diradical, **16**,



**16**

could be weakened by the aryl (or methyl) substitutents of the olefin moiety. Thus, although the cyclobutane-ring compounds, **3a**, **3b**, **3c**, or **3f**, can be relatively stabilized as a result of the intramolecular interactions through π-electrons, the decomposition to the quinone and the olefin might be predominant and no further photochemical reaction to the oxetanol-ring compounds, **2**, could proceed when the cyclobutane-ring compounds, **3**, were irradiated by light of a shorter wavelength.



Scheme 2.

The possible reaction mechanism is summarized in Scheme 2.

## Experimental

*Starting Materials.* *Quinones*: The 2-alkoxy-1,4-naphthoquinones were prepared by the etherification of 2-hydroxy-1,4-naphthoquinone with an appropriate alcohol in the presence of concd sulfuric acid or the boron trifluoride–ether complex, according to the literature; 2-methoxy-1,4-naphthoquinone: mp 178.0—180.5 °C,[18] 2-ethoxy-1,4-naphthoquinone: mp 118.0—119.0 °C,[19] 2-isopropoxy-1,4-naphthoquinone: mp 111.5—112.0 °C,[20] and 2-allyloxy-1,4-naphthoquinone: mp 98.0—100.0 °C.[20]

*Olefins*: 1,1-Di-*p*-tolylethylene was synthesized by the Grignard reaction of *p*-tolylmagnesium bromide and ethyl acetate; then the 1,1-di-*p*-tolylethanol thus produced was subjected to dehydration with 20% sulfuric acid; mp 61.0 °C.[21] The other olefins examined here were commercially available and were purified by distillation before use.

*General Procedures.* 2-Alkoxy-1,4-naphthoquinone (1 mmol) and olefin (2 mmol) were dissolved in benzene (20 ml) and irradiated in a glass tube by means of a high-pressure Hg arc lamp (300 W) through a 5-cm-thick water layer. After the 2-alkoxy-1,4-naphthoquinone had been completely consumed, the benzene was distilled off under reduced pressure. The reaction mixture was purified by chromatography on silica gel and then further purified by recrystallization from an appropriate solvent.

*Identification of the Photo-addition Compounds.* *8-Butyl-2-hydroxy-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one (**2a**)*; colorless oil (yield, 25%). Mass; *m/e*=272 ($M^+$). IR (liq. film); 3480 (OH), 2920, 2840 (CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$): δ; 0.96 (3H, $CH_3$, br t), 1.40 (6H, aliphatic-H, br m), 1.65-1.90 (2H, C-7 $CH_2$, m), 2.84 (1H, C-8 CH, m), 3.28 (1H, C-6 CH, t, *J*=10.0 Hz), 3.80 (1H, OH, s), 4.34, 4.56 (2H, C-10 $CH_2$, AB-q *J*=6.0 Hz), 7.24—7.92 ppm (4H, aromatic-H, m).

*8-Pentyl-2-hydroxy-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one (**2b**)*; white needles from hexane (yield, 50%). Mp 80.0—81.0 °C. Mass; *m/e*=286 ($M^+$). Found: C, 75.78; H, 8.05%. Calcd for $C_{18}H_{22}O_3$: C, 75.49; H, 7.74%. IR (KBr disk); 3360 (OH), 2920, 2840 (CH), 1670 $cm^{-1}$ (C=O). $^1$H-NMR($CCl_4$); δ: 0.92 (3H, $CH_3$, br t), 1.36 (8H, aliphatic-H, m), 1.64—1.90 (2H, C-7 $CH_2$, m), 2.92 (1H, C-8 CH, m,) 3.28 (1H, C-6 CH, t, *J*=10.0 Hz), 3.92 (1H, OH, s), 4.34, 4.56 (2H, C-10 $CH_2$, AB-q, J=6.0 Hz), 7.22—7.96 ppm (4H, aromatic-H, m).

*8-Hexyl-2-hydroxy-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one (**2c**)*; white needles from hexane(yield, 67%); mp 101.0—101.5 °C. Mass; *m/e*=300($M^+$). Found: C, 76.21; H, 8.32%. Calcd for $C_{19}H_{24}O_3$: C, 75.97; H, 8.05%. IR (KBr disk); 3320 (OH), 2920, 2840(CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); δ: 0.92 (3H, $CH_3$, br t), 1.36 (10H, aliphatic-H, m), 1.64—1.90 (2H, C-7 $CH_2$, m), 2.92 (1H, C-8 CH, m), 3.30 (1H, C-6 CH, t, *J*=10.0 Hz), 3.50 (1H, OH, s), 4.38, 4.58 (2H, C-10 $CH_2$, AB-q, *J*=6.0 Hz), 7.28—7.96 ppm (4H, aromatic-H, m).

*8-Heptyl-2-hydroxy-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one (**2d**)*; white needles from benzene–hexane (yield, 48%); mp 84.0—85.0 °C. Mass; *m/e*=314 ($M^+$). IR (KBr disk); 3340 (OH), 2940, 2860 (CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); δ: 0.88 (3H, $CH_3$, br t), 1.10—1.92 (14H, aliphatic-H, m), 2.80 (1H, OH, s), 2.84 (1H, C-8 CH, m), 3.40 (1H, C-6 CH, t, *J*=8.0 Hz), 4.44, 4.62 (2H, C-10 $CH_2$, AB-q, *J*=8.0 Hz), 7.28—8.00 ppm (4H, aromatic-H, m).

*8-Octyl-2-hydroxy-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2e**)*; white needles from petroleum ether (yield, 45 %); mp 110.0—111.0 °C. Mass; *m/e*=328 ($M^+$). IR (KBr disk); 3340 (OH), 2940, 2860 (CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); δ: 0.90 (3H, $CH_3$, t), 1.10—2.00 (16H, aliphatic-H, m), 2.80 (1H, OH, s), 2.82 (1H, C-8 CH, m), 3.46 (1H, C-6 CH, t, *J*=8.0 Hz), 4.56, 4.64(2H, C-10 $CH_2$, AB-q, *J*=8.0 Hz), 7.30—8.04 ppm (4H, aromatic-H, m).

*2-Hydroxy-7,8-tetramethylene-3,4-benzo-1,2-epoxymethanobicyclo-[4.2.0]oct-3-en-5-one(**2f**)*; colorless oil (yield, 39%). Mass; *m/e*=270 ($M^+$). IR (liq. film); 3350 (OH), 2920, 2840 (CH), 1660 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); δ: 0.80—3.25 (10H, aliphatic-H, m), 3.42 (1H, C-6 CH, d, *J*=8.0 Hz), 4.48, 4.64 (2H, C-10 $CH_2$, AB-q, *J*=6.0 Hz), 4.80 (1H, OH, s), 7.24—8.10 ppm (4H, aromatic-H, m).

*7,8-Hexamethylene-2-hydroxy-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2g**)*; white needles (yield, 74%); mp 191.0—198.0 °C (decomp). Mass; *m/e*=298 ($M^+$). IR (KBr disk); 3360 (OH), 2920, 2840 (CH), 1660 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 0.90—3.00 (14H, aliphatic-H, m), 3.04 (1H, C-6 CH, d, $J$=8.0 Hz), 4.52, 4.64 (2H, C-10 $CH_2$, AB-q, $J$=6.0 Hz), 4.72 (1H, OH, s), 7.36—8.12 ppm (4H, aromatic-H, m).

*7,8-(3-Hexenylene)-2-hydroxy-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-ene-5-one(**2h**)*; white crystals (yield, 29%); mp 184.0—186.0 °C (decomp). Mass; *m/e*=296 ($M^+$). IR (KBr disk); 3320(OH), 3000, 2910, 2840 (CH), 1670 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 1.00—2.80 (11H, aliphatic-H and OH, m), 3.16 (1H, C-6 CH, d, $J$=10.0 Hz), 4.68 (2H, C-10 $CH_2$, br s), 5.52 (2H, C-3′ and C-4′ CH′ s, br d), 7.28—7.96 ppm (4H, aromatic-H, m).

*2-Hydroxy-7,8[2′,3′]bicyclo[2.2.1]heptano-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2i**)*; white crystals from chloroform (yield, 50%); mp 214.0—217.0 °C. Mass; *m/e*=282 ($M^+$). Found: C, 76.49; H, 6.63%. Calcd for $C_{18}H_{18}O_3$: C, 75.56; H, 6.44%. IR (KBr disk); 3420 (OH), 2960, 2930, 2880 (CH), 1670 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 1.04—2.16 (7H, aliphatic-H, m), 2.42 (2H, aliphatic-H, m), 2.82 (1H, OH, s), 2.90 (2H, aliphatic-H, m), 4.56, 4.72 (2H, C-10 $CH_2$, AB-q, $J$=6.0 Hz), 7.24—7.92 ppm (4H, aromatic-H, m).

*2-Hydroxy-7,8[2′,3′]bicyclo[2.2.1]hept-5′-eno-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2j**)*; white crystals from chloroform (yield, 35%); mp 199.0—201.0 °C. IR (KBr disk); 3380 (OH), 2960, 2880 (CH), 1665 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 1.22 (3H, aliphatic-H, m), 2.76 (2H, aliphatic-H, m), 2.60 (1H, OH, s), 3.06 (2H, aliphatic-H, m), 4.64, 4.78 (2H, C-10 $CH_2$, AB-q, $J$=6.0 Hz), 6.04 (2H, C-5′ and C-6′ CH′ s, m), 7.24—7.96 ppm (4H, aromatic-H, m).

*2-Hydroxy-indeno[2′,3′-7,8]-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2k**)*; white needles from benzene–petroleum ether (yield, 73%); mp 225.0—227.0 °C (decomp). Mass; *m/e*=304 ($M^+$). Found: C, 79.22; H, 5.28%. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30%. IR (KBr disk); 3320 (OH), 2920 (CH), 1675 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 2.04 (1H, OH, s), 2.64 (1H, C-7 CH, m), 3.04 (2H, C-1′ $CH_2$, dd, $J$=6.0, 10.0 Hz), 3.19 (1H, C-6 CH, m), 4.42(1H, C-8 CH, m), 4.48, 4.76 (2H, C-10 $CH_2$, AB-q, $J$=6.0 Hz), 7.10—8.00 ppm (8H, aromatic-H, m).

*2-Hydroxy-8-phenyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**21=4**)*; white needles from benzene (yield, 69%); mp 164.0—164.5 °C. Mass; *m/e* 292 ($M^+$). Found: C, 78.03; H, 5.45%. Calcd for $C_{19}H_{16}O_3$: C, 78.08; H, 5.52%. IR (KBr disk); 3250 (OH), 2940 (CH), 1675 $cm^{-1}$ (C=O). $UV_{max}$ ($CHCl_3$); 290 nm ($\varepsilon$: $3.0\times10^3$). $^1$H-NMR ($CDCl_3$); $\delta$: 2.16 (1H, C-7 CH, m), 2.58 (1H, C-7 CH, m), 3.22 (1H, OH, s), 3.62 (1H, C-6 CH, dd, $J$=8.0, 12.0 Hz), 4.18 (1H, C-8 CH, dd, $J$=6.0, 10.0 Hz), 4.56, 4.64 (2H, C-10 $CH_2$, AB-q, $J$=6.0 Hz), 7.24—8.10 ppm (9H, aromatic-H, m). $^{13}$C-NMR ($CDCl_3$); $\delta$: 26.63 (t, C-7), 43.44 (d, C-8), 49.63(d, C-6), 70.62 (s, C-1), 82.33 (t, C-10), 90.95 (s, C-2), 126.92 (aromatic-C), 127.05 (aromatic-C), 127.41 (aromatic-C), 128.26 (aromatic-C), 128.56 (aromatic-C), 129.17 (aromatic-C), 130.26 (aromatic-C), 134.93 (aromatic-C), 137.60 (aromatic-C), 143.43 (aromatic-C), 197.24 ppm (s, C-5) (chemical shifts were calibrated from TMS as an internal standard).

*2-Hydroxy-8-methyl-8-phenyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2m**)*; white needles from benzene (yield, 9%); mp 201.0—204.0 °C. Found: C, 78.23; H, 5.88%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%. IR (KBr disk); 3400 (OH), 2950 (CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 1.52 (3H, $CH_3$, s), 2.34 (1H, C-7 CH, dd, $J$=6.0, 10.0 Hz), 2.44 (1H, OH, s), 3.08 (1H, C-7 CH, t, $J$=10.0 Hz), 3.40 (1H, C-6 CH, dd, $J$=6.0, 10.0 Hz), 4.62, 4.70 (2H, C-10 $CH_2$, AB-q, $J$=8.0 Hz), 7.14—8.00 ppm (9H, aromatic-H, m).

*2-Hydroxy-10-methyl-8-phenyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2n**)*; white needles from benzene (yield, 60%); mp 168.0—169.0 °C. Found: C, 78.83; H, 5.73%. Calcd for $C_{20}H_{18}O_3$: C, 78.41, H, 5.92%. IR (KBr disk); 3280 (OH), 2980 (CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 1.16 (3H, $CH_3$, d, $J$=6.0 Hz), 2.16 (1H, C-7 CH, m), 2.58 (1H, C-7 CH, m), 2.94 (1H, OH, s), 3.62 (1H, C-6 CH, dd, $J$=8.0, 12.0 Hz), 4.18 (1H, C-8 CH, dd, $J$=8.0, 12.0 Hz), 4.70 (1H, C-10 CH, q, $J$=6.0 Hz), 7.22—8.10 ppm (9H, aromatic-H, m).

*10,10-Dimethyl-2-hydroxy-8-phenyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2o**)*; white needles from benzene (yield, 7.1%); mp 117.0—118.0 °C. Mass; *m/e*=320 ($M^+$). Found: C, 78.55; H, 6.22%. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29%. IR (KBr disk); 3320 (OH), 2990, 2920 (CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 0.92 (3H, $CH_3$, s), 1.46 (3H, $CH_3$, s), 2.16 (1H, C-7 CH, m), 2.58 (1H, C-7 CH, m), 2.92 (1H, OH, s), 3.62 (1H, C-6 CH, dd, $J$=8.0, 12.0 Hz), 4.18 (1H, C-8 CH, dd, $J$=6.0, 10.0 Hz), 7.20—8.16 ppm (9H, aromatic-H, m).

*2-Hydroxy-8-phenyl-10-vinyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one(**2p**)*; white needles from benzene (yield, 27%); mp 139.0—140.0 °C. Mass; *m/e*=318 ($M^+$). IR (KBr disk); 3280 (OH), 3060, 3020, 2880 (CH), 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 2.16 (1H, C-7 CH, m), 2.58 (1H, C-7 CH, m), 3.00 (1H, OH, s), 3.80 (1H, C-6 CH, dd, 8.0, 10.0 Hz), 4.12 (1H, C-8 CH, dd, $J$=6.0, 10.0 Hz), 5.04—6.16 (4H, vinyl-H and C-10 CH, m), 7.22—8.19 ppm (9H, aromatic-H, m).

*8,8-Diphenyl-1-methoxy-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione(**3a**)*; white crystals (yield, 63%); mp 112.0—113.0 °C. Mass; *m/e*=188 (2-methoxy-1,4-naphthoquinone rest), 180 (1,1-diphenylethylene rest). Found: C, 81.47; H, 5.39%. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47%. IR (KBr disk); 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 3.24 (3H, $OCH_3$, s), 3.40 (3H, C-6 CH and C-7 $CH_2$, m), 6.70—7.90 ppm (14H, aromatic-H, m). $UV_{max}$ ($CCl_4$); 303 nm ($\varepsilon$: $2.0\times10^3$), 312 ($1.9\times10^2$), 352 ($1.7\times10^2$), 365 ($1.5\times10^2$), $UV_{max}$ ($CH_3CN$); 303 nm ($\varepsilon$: $1.9\times10^3$), 312 ($1.7\times10^3$), 349 ($1.5\times10^2$), 361 ($1.4\times10^2$).

*8,8-Di-p-tolyl-1-methoxy-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione(**3b**)*; colorless oil (yield, 71%). Mass; *m/e*=208 (1,1-di-*p*-tolylethylene rest), 188 (2-methoxy-1,4-naphthoquinone rest). IR (KBr disk); 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 2.06 (3H, $CH_3$, s), 2.28 (3H, $CH_3$, s), 3.20 (3H, $OCH_3$, s), 3.16—3.52 (3H, C-6 CH and C-7 $CH_2$, m), 6.75, 7.01 (4H, aromatic-H, AB-q, $J$=10.0 Hz), 7.01, 7.27 (4H, aromatic-H, AB-q, $J$=8.0 Hz), 7.40—7.92 ppm (4H, aromatic-H, m).

*1-Methoxy-8-methyl-8-phenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione(**3c**)*; white crystals (yield, 69%). Mass; *m/e*=306 ($M^+$). Found: C, 78.27; H. 5.50%. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92%. IR (KBr disk); 1685 $cm^{-1}$ (C=O). **3c**-I; $^1$H-NMR ($CCl_4$); $\delta$: 1.60 (3H, $CH_3$, s), 2.44 (2H, C-7 $CH_2$,d, $J$=10.0 Hz), 3.20 (3H, $OCH_3$, s), 3.60 (1H, C-6 CH, t, $J$=10.0 Hz), 6.90—7.97 ppm (9H, aromatic-H, m). **3c**-II; $^1$H-NMR ($CCl_4$); $\delta$: 1.16 (3H, $CH_3$, s), 2.16 (2H, C-7 $CH_2$, m), 3.05 (3H, $OCH_3$, s), 3.40 (1H, C-6 CH, m), 7.14 (5H, aromatic-H, br s), 7.60—8.20 ppm (4H, aromatic-H, m).

*1-Methoxy-8-phenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione(**3d**)*; white crystals (yield, 50% after 89% of quinone was consumed on irradiation with the filter A.); mp 142.5—144.0 °C. Mass; *m/e*=292 ($M^+$). Found: C, 77.79; H, 5.43%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%. IR (KBr disk); 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 2.52, 3.08 (2H, C-7

$CH_2$, m), 3.20 (3H, $OCH_3$, s), 3.70 (1H, C-6 CH, dd, $J$=6.0, 10.0 Hz), 3.92 (1H, C-8 CH, br t, $J$=8.0 Hz), 6.30 (5H, aromatic-H, br s), 7.76—8.32 ppm (4H, aromatic-H, m). $UV_{max}$ ($CCl_4$); 300 nm ($\varepsilon$: $2.8\times10^3$), 310 ($2.6\times10^3$), 343 ($4.5\times10^2$), $UV_{max}$ ($CH_3CN$); 301 nm ($\varepsilon$: $2.6\times10^3$), 310 ($2.4\times10^3$), 339 ($4.5\times10^2$).

*8-Hexyl-1-methoxy-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione (3e)*; colorless oil (yield, 40% after 90% of quinone was consumed on irradiation with the filter A.). Mass; $m/e$=300($M^+$). IR (liq. film); 1690 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 0.98 (3H, $CH_3$, br t, $J$=6.0 Hz), 1.00—1.84 (10H, aliphatic-H, m), 1.92—2.70 (3H, C-7 $CH_2$ and C-8 CH, m), 3.24 (3H, O-$CH_3$, s), 3.42 (1H, C-6 CH, dd, $J$=6.0, 10.0 Hz), 7.20—8.24 ppm (4H, aromatic-H, m). $UV_{max}$ ($CCl_4$); 300 nm ($\varepsilon$: $1.4\times10^3$), 309 ($1.3\times10^3$), 352 ($1.3\times10^2$), $UV_{max}$ ($CH_3CN$); 300 nm ($\varepsilon$: $1.5\times10^3$), 308 ($1.4\times10^3$), 349 ($1.7\times10^2$).

*1-Ethoxy-8,8-diphenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione (3f)*; white crystals (yield, 60%); mp 112.0—113.0 °C. Mass; $m/e$=382 ($M^+$). Found: C, 81.49; H, 5.80%. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80%. IR (KBr disk); 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 1.18 (3H, $CH_3$, t, $J$=8.0 Hz), 3.40 (2H, $CH_2$, q, $J$=8.0 Hz), 3.38 (3H, C-6 CH and C-7 $CH_2$, m), 6.72—7.90 ppm (14H, aromatic-H, m).

*1-Isopropoxy-8-phenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione (3g)*; white needles (yield, 41%); mp 91.0—92.0 °C. Mass; $m/e$=320 ($M^+$). Found: C, 79.07; H, 5.85%. Calcd for $C_{21}H_{20}O_3$: C, 78.75; H, 6.25%. IR (KBr disk); 2970 (CH), 1690, 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 0.68 (3H, $CH_3$, d, $J$=6.0 Hz), 0.90 (3H, $CH_3$, d, $J$=6.0 Hz), 2.14 (1H, C-7 CH, m), 2.83 (1H, C-7 CH, m), 3.60—4.00 (3H, O-CH, C-6 CH, and C-8 CH' s, m), 7.24 (5H, aromatic-H, br s), 7.60—8.24 ppm (4H, aromatic-H, m). $UV_{max}$ ($CHCl_3$); 300 nm ($\varepsilon$: $2.3\times10^3$), 310 ($1.8\times10^3$), 338 ($3.3\times10^2$).

*The Acetylation of the Photo-addition Compound, 4.* The acetyl derivative **6** was prepared by standing the photo-addition compound, **4**, (115 mg) in acetic anhydride (5 ml) containing few drops of pyridine for 3 h at room temperature, and by then pouring the mixture into cold water (10 ml). After extraction with ether and subsequent purification using thin-layer chromatography on silica gel, 2-acetoxy-8-phenyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one, **6**, was obtained as white plates (110 mg; yield, 83%); mp 92.0—93.0 °C from petroleum ether. Mass; $m/e$=334 ($M^+$). IR (KBr disk); 1740, 1682 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 2.13 (3H, $OCOCH_3$, s), 2.60 (2H, C-7 $CH_2$, dd, $J$=6.0, 8.0 Hz), 3.56 (1H, C-6 CH, t, $J$=8.0 Hz), 3.84 (1H, C-8 CH, t, $J$=6.0 Hz), 4.52, 4.84 (2H, C-10 $CH_2$, AB-q, $J$=6.0 Hz), 7.30 (5H, aromatic-H, br s), 7.20—8.05 ppm (4H, aromatic-H, m).

*The Acid-catalyzed Decomposition of the Photo-addition Compound, 4.* The acid-catalyzed decomposition was completed by treating the photo-addition compound, **4** (200 mg) in chloroform (15 ml) with a few drops of concd hydrochloric acid or concd sulfuric acid at room temperature for 8 h. After the concentration of the reaction mixture and purification using thin-layer chromatography on silica gel, two isomers of 7-phenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione, **7a** (61 mg; yield, 38%) and **7b** (35 mg; yield, 22%), were isolated as white crystals; **7a**; mp 112.0—115.0 °C. Mass; $m/e$=262 ($M^+$). IR (KBr disk); 1690 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 2.70 (2H, C-8 $CH_2$, m), 3.40—3.70 (3H, C-1, C-6 and C-7 CH' s, m), 7.16 (5H, aromatic-H, br s), 7.92—8.10 ppm (4H, aromatic-H, m). **7b**; mp 147.0—148.0 °C. Mass; $m/e$=262 ($M^+$). IR (KBr disk); 1680 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 2.70—3.20 (2H, C-8 $CH_2$, m), 3.60—4.40 (3H, C-1, C-6, and C-7 CH's, m), 6.90—7.40 (5H, aromatic-H, m), 7.60—8.20 ppm (4H, aromatic-H, m).

*The Photochemical Reaction of 1,4-Naphthoquinone with Styrene.* A benzene solution (20 ml) of 1,4-naphthoquinone (158 mg) and styrene (210 mg) was submitted to the irradiation of a high-pressure Hg arc lamp. After the complete consumption of the quinone, **7a** (118 mg; yield, 45%) and **7b** (28 mg; yield, 11%) were isolated from the reaction mixture through purification by thin-layer chromatography on silica gel.

*The Acetylation of 7a or 7b.* 3,8-Diacetoxy-1-phenyl-1,2-dihydrocyclobuta[*b*]naphthalene, **8**, was prepared by refluxing a mixture of **7a** (or **7b**) (70 mg) and sodium acetate (200 mg) dissolved in acetic anhydride (15 ml) for 3 h. **8** was thus obtained in a 57% yield (53 mg) as white needles from benzene-hexane; mp 135.0 °C. Mass; $m/e$=346 ($M^+$). Found: C, 76.10; H, 5.38%. Calcd for $C_{22}H_{18}O_4$: C, 76.28; H, 5.25%. IR (KBr disk); 1750 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 2.16 (3H, $COCH_3$, s), 2.42 (3H, $COCH_3$, s), 3.18 (1H, C-2 CH, dd, $J$=4.0 14.0 Hz), 3.82 (1H, C-2 CH, dd, $J$=8.0, 14.0 Hz), 4.78 (1H, C-1 CH, dd, $J$=4.0, 8.0 Hz), 7.24 (5H, aromatic-H, br s), 7.36—8.04 ppm (4H, aromatic-H,m).

*The Bromination of the Photo-addition compound, 4.* Bromine (100 mg) was added to a chloform solution (25 ml) of the photo-addition compound, **4** (300 mg), after which the mixture was allowed to stand for 15 h at room temperature. Two products, **9** and **10**, were isolated in 54% (189 mg) and 32% (122 mg) yields respectively after the purification of the reaction mixture using thin-layer chromatography on silica gel. 1-Bromo-7-phenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione (**9**); white crystals from benzene-peroleum ether; mp 136.0—137.0 °C. Mass; $m/e$=342, 340 ($M^+$). IR (KBr disk); 1695 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 3.20—3.50 (2H, C-7 CH and C-8 CH, m), 3.78 (1H, C-8 CH, dd, $J$=8.0, 12.0 Hz), 4.74 (1H, C-6 CH, d, $J$=8.0 Hz), 7.10-7.50 (5H, aromatic-H,m), 7.70—8.40 ppm (4H, aromatic-H, m). 6-Bromo-2-hydroxy-8-phenyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one (**10**); white crystals. Mass; $m/e$=372, 370 ($M^+$). IR (KBr disk); 3400 (OH), 1670 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 2.94 (1H, C-7 CH, dd, $J$=10.0, 12.0 Hz), 3.10 (1H, OH, s), 3.26 (1H, C-7 CH, dd, $J$=8.0, 12.0 Hz), 3.92 (1H, C-8 CH, dd, $J$=8.0, 10.0 Hz), 4.64, 4.74 (2H, C-10 $CH_2$, AB-q, $J$=8.0 Hz), 7.30—8.00 ppm (9H, aromatic-H, m).

*The Bromination of 6.* By treating a chloroform solution (10 ml) of **6** (110 mg) with bromine (30 mg) for 15 h at room temperature, **9** (65 mg; yield, 50%) and **11** (49 mg; yield, 36 %) were obtained: 2-acetoxy-6-bromo-8-phenyl-3,4-benzo-1,2-epoxymethanobicyclo[4.2.0]oct-3-en-5-one (**11**); white needles from benzene-petroleum ether; mp 138.0—138.5 °C. Mass; $m/e$=414, 412 ($M^+$). IR (KBr disk); 1740, 1690 $cm^{-1}$ (C=O). $^1$H-NMR ($CDCl_3$); $\delta$: 2.84 (3H, $COCH_3$, s), 2.80 (1H, C-7 CH, dd, $J$=8.0, 12.0 Hz), 3.42 (1H, C-7 CH, dd, $J$=8.0, 12.0 Hz), 3.92 (1H, C-8 CH, t, $J$=8.0 Hz), 4.68, 4.78 (2H, C-10 $CH_2$, AB-q, $J$=6.0 Hz), 7.26 (5H, aromatic-H, br s), 7.10—7.90 ppm (4H, aromatic-H, m). **11** was also isolated from the reaction mixture of the acetylation of **10** by acetic anhydride-pyridine.

*The Bromination of 7b.* **9** was also identified as one of the reaction products of **7b** (115 mg) with bromine (100 mg) in chloroform (10 ml) at room temperature for 20 h.

*The Clemmensen Reduction of the Photo-addition Compound, 4.* The photo-addition compound, **4** (500 mg), toluene (5 ml), amalgamated zinc (10 g), and concd hydrochloric acid (12 ml) were heated for 8 h. Three reaction products, **12**, **13**, and **14**, were isolated from the reaction mixture using thin-layer chromatography on silica gel in 17% (42 mg), 7% (20 mg), and 12% (37 mg) yields respectively; 8-methyl-1-phenyl-1,2-dihydrocyclobuta[*b*]naphthalene (**12**); colorless oil. Mass; $m/e$=244 ($M^+$). IR (liq. film); no OH or C=O. $^1$H-NMR ($CCl_4$); $\delta$: 2.56 (3H, $CH_3$, s), 2.70—3.20 (3H, C-1 CH and C-2 $CH_2$, m), 7.60 (5H, aromatic-H, br s), 7.10—8.00 ppm

(5H, aromatic-H, m). $UV_{max}$ ($CHCl_3$); 243 nm ($\varepsilon$: $7.9\times10^3$), 276 ($5.0\times10^3$), 307 ($1.7\times10^3$), 322 ($1.4\times10^3$). 4-Phenyl-3,4-dihydro-1H-oxeto[2′,3′: 3,4]naphtho[1,2-*b*]furan (**13**); white needles from benzene–petroleum ether; mp 137.0—139.0 °C. Mass; *m/e*=274 ($M^+$). Found: C, 83.06; H, 5.35 %. Calcd for $C_{19}H_{14}O_2$: C, 83.20; H, 5.15%. IR (KBr disk); no OH or C=O. $^1$H-NMR ($CDCl_3$); $\delta$: 3.14 (2H, C-3 $CH_2$, m), 4.82 (1H, C-4 CH, dd, $J$=4.0, 10.0 Hz), 5.44 (2H, C-1 $CH_2$, AB-q, $J$=15.0 Hz), 7.14—7.90 ppm (9H, aromatic-H, m). $UV_{max}$ ($CHCl_3$); 242 nm ($\varepsilon$: $6.9\times10^3$), 266 ($4.9\times10^3$), 274 ($6.1\times10^3$), 280 ($6.3\times10^3$), 291 ($4.8\times10^3$), 307 ($8.8\times10^2$), 313 ($5.7\times10^2$), 322 ($6.6\times10^2$). 2-(2-Hydroxy-2-phenylethyl)-4-methylnaphthalene-1,3-diol (**14**); colorless oil. Mass; *m/e*=276 ($M^+-H_2O$). IR (liq. film); 3850, 3400 $cm^{-1}$ (OH). $^1$H-NMR ($CCl_4$); $\delta$: 2.56 (3H, $CH_3$, s), 3.18 (2H, CH, d, $J$=6.0 Hz), 4.82 (1H, CH, t, $J$=6.0 Hz), 7.10—8.00 ppm (9H, aromatic-H, m). $UV_{max}$ ($CHCl_3$); 246 nm ($\varepsilon$: $7.2\times10^3$), 275 ($4.4\times10^3$), 283 ($3.8\times10^3$), 321 ($1.2\times10^3$).

*The Thermal Decomposition of* ***12***. The thermal decomposition of **12** at 500 °C for 20 min in a sealed tube gave 1-methylnaphthalene, which was identified by gas-liquid-partition chromatography.

*The Acetylation of* ***14***. A monoacetylated product, **15**, was identified through the acetylation of **14** with sodium acetate–acetic anhydride: 4-Acetoxy-5-methyl-2-phenyl-2,3-dihydronaphthalene[1,2-b]furan (**15**); Mass; *m/e*=328 ($M^+$). IR (liq, film); 1730 $cm^{-1}$ (C=O). $^1$H-NMR ($CCl_4$); $\delta$: 2.00 (3H, $COCH_3$, s), 2.56 (3H, $CH_3$, s), 3.18, 3.46 (2H, $CH_2$, d×AB-q, $J$=6.0, 12.0 Hz), 5.96 (1H, CH, t, $J$=8.0 Hz), 7.00—8.10 ppm (9H, aromatic-H, m).

*The Thermal Decomposition of* ***3a***. A 0.04 M-$CCl_4$ solution of **3a** was submitted to thermal decomposition at 75±1 °C; the rate was followed by means of $^1$H-NMR. The half-life of **3a** was estimated to be about 92 min.

*The Determination of the Quantum Efficiency*. The light source was a high-pressure Hg arc lamp (300 W) with the filter, A. Irradiation carried out at a constant temperature (16±0.5 °C). The quanta of light absorbed by the reaction mixture was calibrated using an aqueous solution of potassium ferroxalate as a chemical actinometer;[22] it was estimated to be $2.07\times10^{-5}$ mol/10.0 ml/min. The reaction mixture submitted to the measurement was a benzene solution of $2.00\times10^{-2}$ mol/l of 2-methoxy-1,4-naphthoquinone and $4.00\times10^{-2}$ mol/l of styrene. The quantum efficiency was calculated for the disappeaance of 2-methoxy-1,4-naphthoquinone and was estimated to be 0.18.

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