Photo-addition Reaction of 1,4-Naphthoquinone with Olefins.[1] Formation of 2:1 Addition Compounds

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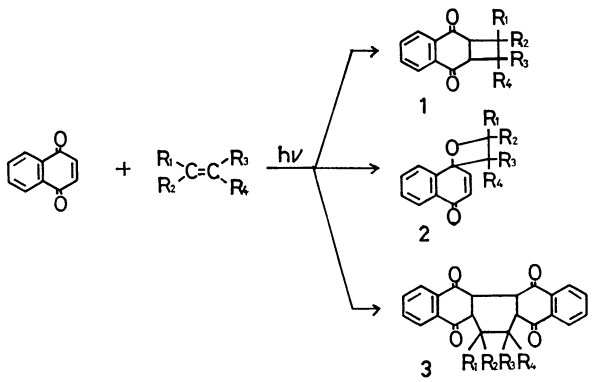
A novel type of the photo-addition compound, 5,8,13,14-tetraoxo-5,5a,6, 7,7a,8,13,13a,13b,14-decahydropentaphene derivatives (**3**), consisting of two molecules of 1,4-naphthoquinone and one molecule of an olefin was obtained in the photochemical reaction of 1,4-naphthoquinone with olefins. Its structure was determined from spectral data as well as results obtained from the chemical reactions. Olefins which give this type of photo-addition compound are characterized by their bicyclo-ring systems containing considerable ring strains. The reaction mechanism for formation of the compound was discussed in terms of the ring strains of olefins and the nature of the photo-excited 1,4-naphthoquinone.

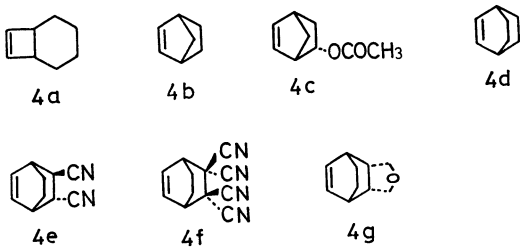
Photochemistry has provided versatile routes to many elegant compounds which otherwise are difficult to prepare.[2] From synthetic and theoretical viewpoints, elucidation of the photochemical behaviour of quinones would be fruitful since quinones and related compounds play an important role in natural environments. Several workers[3,4] have investigated the photochemical reaction of 1,4-naphthoquinone with olefins. 1,4-Naphthoquinone has been found to give 1:1 photo-addition compounds with olefins, besides the photo-reduction products of 1,4-naphthoquinone such as 1,4-naphthohydroquinone and 1,4-naphthoquinhydrones. The photo-addition compounds reported



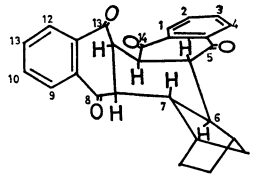
so far were classified into structural types **1** and **2**.[3,4] We have now been able to isolate a novel type of 2:1 photo-addition compound **3** in the photochemical reaction of 1,4-naphthoquinone with olefins characterized by their bicyclo-ring systems containing considerable ring strains. The photo-addition compound was confirmed to consist of two molecules of 1,4-naphthoquinone and one molecule of an olefin and to have the structure **3** by inspection of the spectral data and from the Baeyer-Villiger oxidation of the addition compound.[1] In this report the reaction mechanism for the formation of this novel photo-addition compound **3** is discussed on the basis of product analyses and quenching experiments.

Results and Discussion

Photo-addition Compounds Obtained in the Photochemical Reaction of 1,4-Naphthoquinone with Olefins. A benzene solution of 1,4-naphthoquinone was subjected to photochemical reaction of olefins on irradiation with a high pressure Hg arc lamp. Olefins examined here were all characterized by their strained bicyclo-ring systems, such as bicyclo[4.2.0]oct-7-ene **4a**,[5] bicyclo-[2.2.1]hept-2-ene **4b**, *endo*-2-acetoxybicyclo[2.2.1]hept-5-ene **4c**,[6] bicyclo[2.2.2]oct-2-ene **4d**, *trans*-2,3-dicyanobicylo[2.2.2]oct-5-ene **4e**,[7] 2,2,3,3-tetracyanobicyclo-[2.2.2]oct-5-ene **4f**[8] and 4-oxatricyclo[2.2.5^{2,6}]undec-8-ene **4g**.



With olefins **4a**, **4b** and **4d**, the photochemical reaction of 1,4-naphthoquinone was found to produce the photo-addition compounds without the formation of 1,4-naphthohydroquinone or 1,4-naphthoquinhydrones. The photo-addition compounds isolated were subjected to further examination for determination of their structures. From the results the photo-addition compounds could be classified into three structural types **1**, **2** and **3**. Structure **3** was determined by the isolation of methyl ester of cyclohexane tetracarboxylic acid derivatives **5** when the photo-addition compound **3b** was subjected to oxidative degradation by perfluoroacetic acid and subsequent esterification with diazomethane.[1] The photo-addition compound **3** is outstanding, being constructed from two molecules of 1,4-naphthoquinone and one molecule of an olefin, while **1** and **2** are each composed of one moelcule of 1,4-naphthoquinone and an olefin. Compound **3** was



3b

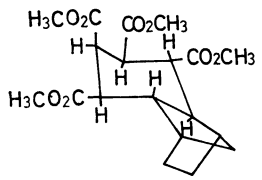


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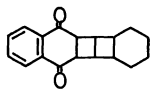
Table 1. Yields of the photo-addition compounds[a]

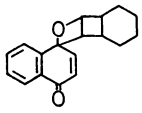
Olefin	The photo-addition compounds %)[c]		
	1	2	3
4a	—(**1a**)	—(**2a**)	1(**3a**)
4b	[b](**1b**)	6(**2b**)	10(**3b**)
4d	9(**1d**)	trace(**2d**)	4(**3d**)

a) The yields were estimated on the basis of the amount of quinones consumed (30 °C). b) **1b** was identified only in the presence of fumaronitrile in the reaction system. c) The other products were unidentified resionous matters.

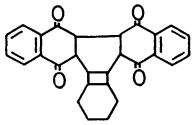
first isolated in this work. The distributions and the yields of these photo-addition products are summarized in Table 1.



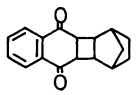
1a



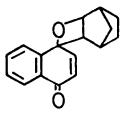
2a



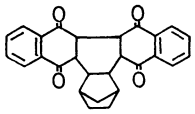
3a



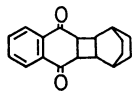
1b



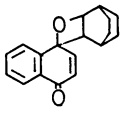
2b



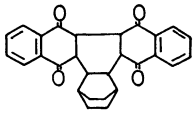
3b



1d

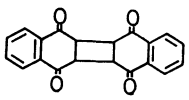


2d



3d

Olefin **4g** was found to react as a reducing agent due to its active hydrogen atoms to yield 1,4-naphthoquinhydrones, no photo-addition products being isolated. With olefins characterized by having electron withdrawing substituents such as **4c**, **4e** and **4f**, 1,4-naphthoquinone could not undergo the photo-addition reaction, but the photo-dimerization of 1,4-naphthoquinone proceeded to yield its dimer **6**[9] as a sole reaction product. For elucidation of the mechanism for formation of the photo-addition compounds **1**, **2** and especially **3**, the behaviour of photo-excited 1,4-naphthoquinone was investigated.



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Quantum Yields and Relation to Their Ring Strains in Olefins. Quantum yields of the cycloaddition were measured in the reaction of 1,4-naphthoquinone with **4b** and **4d** on irradiating (λ>300 nm) the degassed solution of 1,4-naphthoquinone and an olefin at room temperature using potassium ferrioxalate as a chemical actinometer. The results are summarized in Table 2. Although the quantum yields for the formation of **3b** and **3d** are comparable, it should be noted that the quantum yield for the formation of **1d**+**2d** is about five times greater than that of **1b**+**2b**, and the quantum yield for the formation of **2b** is about ten times greater than that of **2d**. Taking into account the fact that olefin **4a** gives none of **1a** or **2a**, we find that the formation of **1** or **2** is much influenced by the nature of olefins subjected to the reaction, particularly by the ring strains in olefins. Coupling constants of olefinic protons with ^{13}C ($J_{^{13}C-H}$) are the direct measure of the ring strains of the double bonds in olefins. They are given in Table 3 together with the % *s*-character

Table 2. Quantum yields for the formation of photo-addition compounds[a,b]

Olefin	The photo-addition compounds		
	1	2	3
4b	~0 (**1b**)	5.6×10^{-3}(**2b**)	8.8×10^{-3}(**3b**)
4d	26.0×10^{-3}(**1d**)	0.5×10^{-3}(**2d**)	9.0×10^{-3}(**3d**)

a) The quantum yields were extrapolated to zero hours of the reaction. b) The quantum yields were measured at 30 °C.

Table 3. Coupling constants of ^{13}C–H and its % *s*-character

Olefin	$J_{^{13}C-H}$	% *s*-character
4a	170 Hz	34
4b	165 Hz[a]	33
4d	158 Hz	32

a) K. Tori, R. Muneyuki, H. Tanida, *Can. J. Chem.*, **14**, 3142 (1963).

of the C–H bonds estimated therefrom. The $J_{^{13}C-H}$ in **4d** (158 Hz) is comparable to that in cyclohexane ($J_{^{13}C-H}$=157 Hz),[10] which is estimated to have no ring strains. It was deduced that the formation of the cyclobutane or oxetane type of compound **1** or **2** becomes less favorable as the ring strains in olefins increase; that is, none of **1a** or **2a** could be identified in the photochemical reaction of 1,4-naphthoquinone with **4a**, which has the greatest value of $J_{^{13}C-H}$ and is consequently of the greatest ring strain among the olefins examined here. On the other hand, no further chemical change could be observed on irradiating the benzene solution of **1b** in the presence of excess 1,4-naphthoquinone nor on irradiating the benzene solution of the dimer **6** in the presence of excess bicyclo[2.2.1]-hept-2-ene **4b**. From these results neither **1b** nor **6** could be the precursor of **3b**. Dependence of the yields of the photo-addition compounds **2b** and **3b** on the concentration of bicyclo[2.2.1]hept-2-ene **4b** was measured (Fig. 1). As the concentration of bicyclo-[2.2.1]hept-2-ene increases, the yields of both **2b** and **3b** increase, while the amount of the dimer **6** is depressed. Moreover, it is seen that the ratio **3b**/**2b** is nearly constant irrespective of the concentration of bicyclo-[2.2.1]hept-2-ene. The results exclude the possibility of simultaneous formation of **3b** from two molecules of 1,4-naphthoquinone and one molecule of bicyclo-[2.2.1]hept-2-ene, and suggest that the similar types of

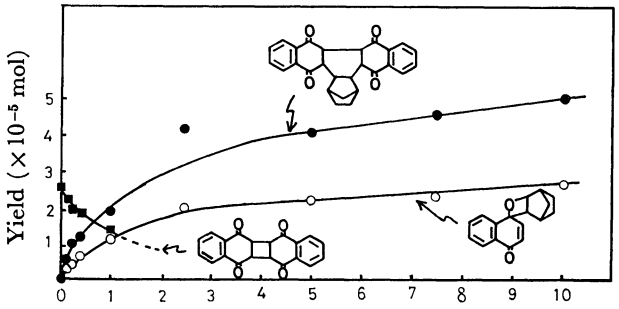
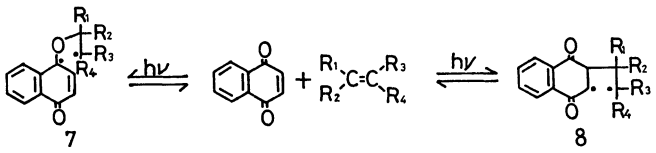


Fig. 1. Dependence of the yields of the photo-addition compounds on the concentration of bicyclo[2.2.1]hept-2-ene.
The 0.100 M-benzene solution of 1,4-naphthoquinone is submitted to the photochemical reaction (30 °C).

reaction intermediates are concerned with the formation of **2b** and **3b**. Consequently it can be deduced that the reaction intermediates for the formation of **2b** and **3b** are each composed of one molecule of 1,4-naphthoquinone and bicyclo[2.2.1]hept-2-ene as illustrated by **7** and **8**, respectively. The effects of higher



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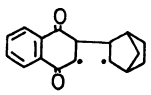
ring strains in olefin **4** on the formation of **2** might be explained, if we assume that compound **2** is produced *via* the ring closure of diradical **7** (see Tables 1 and 2), and compounds **1** and **3** *via* diradical **8**. The larger ring strains in olefins would be less favourable for the ring closure to yield **1** and **2**, because of the lack of the energy relaxation mode to bonding vibration or ring fluctuation. This would result in the longer life-time of the diradicals to meet other molecules or to decompose to the starting quinone and olefin. The fairly large steric repulsion for the ring closure may be another factor to lead to the longer life-time of the diradicals. Thus, **3** may be formed. Actually, the relative yield of **3** in each reaction is high in the order of the higher ring strain of olefins, and the cyclobutane type of **1** could be isolated only in the reaction of 1,4-naphthoquinone with **4d**, which would contain the least ring strains of the three olefins examined. The unidentified resinous matter, *i.e.* polymers produced in the highest yield of the products, may be formed on the same basis as described above. The smaller yield of **2d** compared with **2b** could result from the larger steric hindrance against the ring closure due to bulkier bicyclo[2.2.2]-oct-2-ene moiety. In the presence of fumaronitrile, however, the excess energy in **8b** would transfer to fumaronitrile to produced **1b** even if the minor portion of **8b** is concerned. Details of the photo-excited states



8b

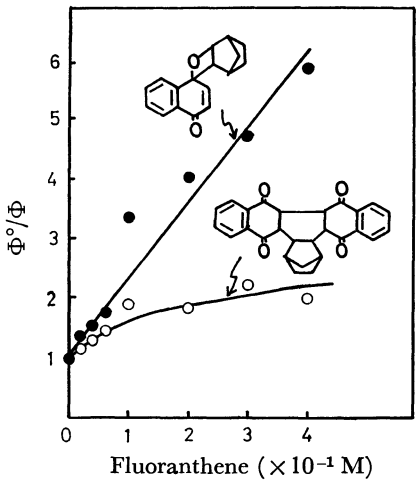


Fig. 2. Stern-Volmer plots quenched by fluoranthene in the photochemical reaction of 1,4-naphthoquinone with bicyclo[2.2.1]hept-2-ene (30 °C).

of 1,4-naphthoquinone to produce the diradical intermediates such as **7** or **8**, and subsequently to yield the photo-addition compounds are discussed in the following.

Correlation between the Reactivity and the Multiplicity of the Photo-excited 1,4-Naphthoquinone. The triplet energy of 1,4-naphthoquinone has been estimated to be 58 kcal/mol.[11] Fluoranthene could quench the triplet excited state of 1,4-naphthoquinone since E_T-value for fluoranthene has been estimated to be 54 kcal/mol.[12a] Dependence of the quantum yields for the formation of **2b** and **3b** on the concentration of fluoranthene as a quencher was estimated. The Stern-Volmer plots are shown in Fig. 2, in which the straight line for the formation of **2b** indicates that **2b** is formed through the triplet excited state of 1,4-naphthoquinone. This agrees with the findings that the oxetanes are formed *via* the triplet excited states in the photochemical reaction of benzophenone[12b] or *p*-benzoquinone[16] with olefins. Scheme 1 shows the reaction paths for the formation of oxetanes *via* diradical **7**, involving unimolecular deactivation of the excited state of 1,4-

$$D \xrightarrow{h\nu} {}^1D^*$$

$${}^1D^* \xrightarrow{k_f,\ k_d^S} D$$

$${}^1D^* \xrightarrow{k_{ST}} {}^3D^*$$

$${}^3D^* \xrightarrow{k_d^T} D$$

$${}^3D^* + A \xrightarrow{k_a} D\text{-}A$$

$$D\text{-}A \xrightarrow{k_r} Ox$$

$$D\text{-}A \xrightarrow{k_d'} D + A$$

$${}^3D^* + Q \xrightarrow{k_q} D + {}^3Q^*$$

D : 1,4-Naphthoquinone
A : Bicyclo[2.2.1]hept-2-ene (**4b**)
Q : Fluoranthene
Ox: Spiro-oxetane (**2b**)

Scheme 1.

naphthoquinone (k_f, k_d^s, k_p^T), intersystem crossing (k_{ST}), formation of diradical intermediate **7** (k_a), formation of oxetane (k_r) and dissociation of diradical intermediate **7** (k_d') and the triplet quenching of 1,4-naphthoquinone by fluoranthene (k_q). The quantum yields for the formation of oxetanes are expressed as Φ_{ox} and/or Φ_{ox}°, corresponding to whether in the presence and/or absence of quencher, respectively (Eqs. (1) and/or (2)).

$$\frac{1}{\Phi_{ox}} = \frac{1}{\Phi_{ST}}\left(1+\frac{k_d'}{k_r}\right)\left(1+\frac{k_d^T+k_q[Q]}{k_a[A]}\right) \quad (1)$$

$$\frac{1}{\Phi_{ox}^{\circ}} = \frac{1}{\Phi_{ST}}\left(1+\frac{k_d'}{k_r}\right)\left(1+\frac{k_d^T}{k_a[A]}\right) \quad (2)$$

The relative ratio $\Phi_{ox}^{\circ}/\Phi_{ox}$ can be derived from Eqs. (1) and (2) as follows.

$$\frac{\Phi_{ox}^{\circ}}{\Phi_{ox}} = 1 + \frac{k_q[Q]}{k_a[A]+k_d^T} = 1 + k_q\tau[Q] \quad (3)$$

τ: the life-time of the tripelt state of 1,4-naphthoquinone in the absence of a quencher.

From the slope and the intercept of the plots shown in Fig. 2 and $\Phi_{ox}^{\circ}=0.0056$, the following rate constants and the ratio can be evaluated; $k_a=2.0\times10^6$ $M^{-1}s^{-1}$, $k_d^T=3.0\times10^7$ s^{-1}, $k_d'/k_r=100$, assuming $\Phi_{ST}\simeq1$[13] and $k_q=5.0\times10^9$ $M^{-1}s^{-1}$ for the benzene solution at 25 °C[14]. These values are compatible to those obtained in the photochemical reaction of benzophenone with furan.[15] The state diagram estimated for the formation of oxetanes is given in Fig. 3.

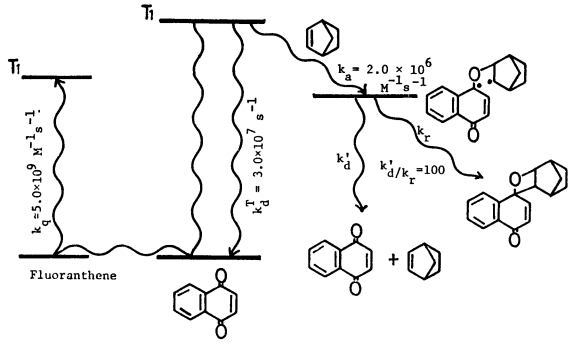


Fig. 3. The state diagram for the formation of spiro-oxetane (30 °C).

The formation of **3b**, on the other hand, is expected to proceed through both the singlet excited state and the triplet excited state of 1,4-naphthoquinone since the Stern-Volmer plots for the formation of **3b** does not give a straight line; it can be estimated that about 60% of the reaction proceeds through the singlet excited state of 1,4-naphthoquinone and the residual 40% through the triplet state since the ratio of quantum yields approaches a constant value (2.5) with increasing concentration of the quencher. It could be assumed that the singlet excited state of 1,4-naphthoquinone reacts also with olefins to give the photo-addition compound and this could be substantiated further by the following results.

Quenching of the Fluorescene of 1,4-Naphthoquinone by Olefins. The fluorescene of 1,4-naphthoquinone at 77 K and at room temperature was observed when

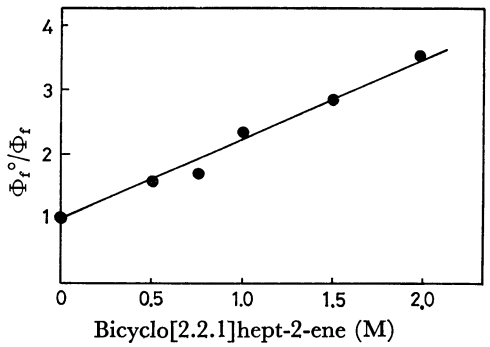


Fig. 4. Quenching of the fluorescene of 1,4-naphthoquinone by bicyclo[2.2.1]hept-2-ene (20 °C).

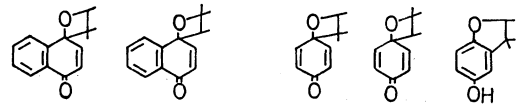
degassed solution of 1,4-naphthoquinone of ether–ethyl alcohol (vol/vol=1/1) was irradiated by light at 333 nm. The intensity of fluorescene was measured at λ_{max}=400 nm in the absence and in the presence of bicyclo[2.2.2]-hept-2-ene (Fig. 4). From the linear relationship observed, it is concluded that the singlet excited state of 1,4-naphthoquinone can be quenched by bicyclo[2.2.1]-hept-2-ene. This is consistent with the findings that the formation of **3b** proceeds partly through the singlet excited state of 1,4-naphthoquinone.

TABLE 4. QUANTUM YIELDS FOR THE FORMATION OF **2b** AND **3b** THROUGH THE EXCITATION OF n–π^* AND π–π^* TRANSITIONS (measured at 30 °C)

Photo-addition compound	Φ_{total} [a]	Φ_{333} [b]	Φ_{420} [c]
2b	8.8×10^{-3}	8.1×10^{-3}	7.0×10^{-3}
3b	5.6×10^{-3}	4.4×10^{-3}	4.4×10^{-3}

a) Excited through both n-π^* and π-π^* transitions. b) Excited through π-π^* transition with use of a Corning CS-7-54 filter. c) Excited through n-π^* transition with use of a Toshiba VY-42 filter.

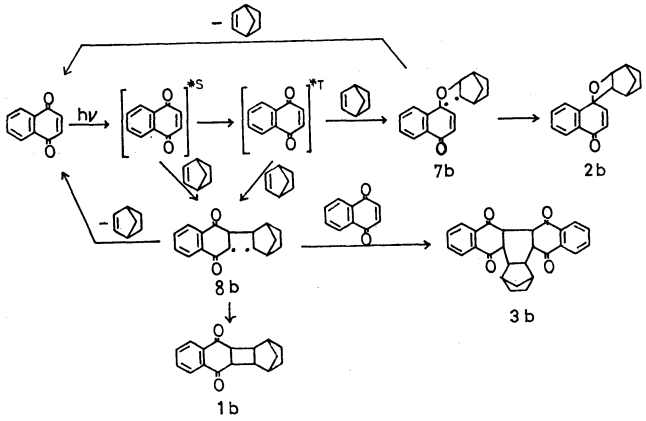
Mixing between the π-π^* Excited States of 1,4-Naphthoquinone. The benzene solution of 1,4-naphthoquinone shows two characteristic absorption bands in the region of wavelength greater than 300 nm. The bands, λ_{max}=333 nm and 420 nm, can be assigned to π-π^* and n-π^* transitions, respectively. The quantum yields for the formation of **2b** and **3b** were measured in each case when 1,4-naphthoquinone was excited through π-π^* and n-π^* transitions to react with bicyclo-[2.2.1]hept-2-ene (Table 4). The π-π^* excitation of 1,4-naphthoquinone was as equally effective as the n-π^* excitation for the formation of **2b** and **3b**. These results suggest that the lower excited singlet or triplet state would be responsible to the formation of **3b**, irrespective of the bands used for the excitation. However, the lower triplet excited state would contribute predominantly to the formation of **2b**. From the results the mixting between the π-π^* and n-π^* excited states of 1,4-naphthoquinone seems to exist to a considerable extent. This is not the case in the photo-excited states of *p*-benzoquinone. The suggestion was supported further by the following facts: in the photochemical reaction of 1,4-naphthoquinone with 2-methylbut-2-ene the oxetanes isolated are found to be a non-stereo-



9a 9b 10a 10b 11

selective mixture of **9a** and **9b** (**9a**/**9b**=1.3); in the photochemical reaction of *p*-benzoquinone with 2-methylbut-2-ene, only one isomer **10a** of the possible two isomers and its further rearrangement product **11** could be isolated stereoselectively from the reaction mixture, but none of the other isomer **10b**.[16] The lack of stereoselectivity in the photochemical reaction of 1,4-naphthoquinone with 2-methylbut-2-ene is attributable solely to the smaller degree of electron defficiency of oxygen atom in the n-π^* excited state of 1,4-naphthoquinone, *i.e.*, indication of larger mixing of the n-π^* state with π-π^* state than in the case of *p*-benzoquinone, since the stability of the diradical intermediates **7** to form **9a** and **9b**, or **10a** and **10b** could be estimated in the same order.

We can thus formulate the reaction of 1,4-naphthoquinone with bicyclo[2.2.1]hept-2-ene as shown in Scheme 2. A novel type of photo-addition compound **3** derived from the other higher strained olefins would be formed following a similar reaction scheme.



Scheme 2.

Experimental

Materials. 1,4-Naphthoquinone, *p*-benzoquinone, bicyclo[2.2.1]hept-2-ene (**4b**) and fluoranthene were used after sublimation of commercial reagents of guaranteed grade. Bicyclo[2.2.2]oct-2-ene (**4d**) and 2-methylbut-2-ene were subjected to the reaction without further purification. Bicyclo-[4.2.0]oct-7-ene (**4a**), *endo*-2-acetoxybicylo[2.2.1]hept-5-ene (**4c**), *trans*-2,3-dicyanobicyclo[2.2.2]oct-5-ene (**4e**) and 2,2,3,3-tetracyanobicyclo[2.2.2]oct-5-ene (**4f**) were synthesized according to reported method.[5-8]

4-Oxatricyclo[2.2.5^{2,6}]undec-8-ene (4g); *endo-cis*-Bicyclo[2.2.2]-oct-5-ene-2,3-dicarboxylic anhydride[17] was treated with lithium aluminum hydride in dry ether for conversion into *endo-cis*-2,3-bis(hydroxymethyl)bicyclo[2.2.2]oct-5-ene. *p*-Toluenesulfonyl chloride (29.5 g) was added to 100 ml of pyridine solution containing 6.5 g of *endo-cis*-2,3-bis(hydroxymethyl)-bicyclo[2.2.2]oct-5-ene in an ice-cooled bath with stirring, then allowed to stand for two days at room temperature. The pyridine solution was poured into ice water (200 ml) and extracted twice with 75 ml of ether. The extract was washed twice with cold dilute hydrochloric acid solution, once with water and then dried over anhydrous sodium sulfate. Oily ditosylate was obtained after ether had been evaporated. The crude ditosylate was reduced with lithium aluminum hydride. After the work-up, the cyclic ether (**4g**) was distilled under a reduced pressure, yield: 4.0 g (76%): bp 134.5—135.6 °C (80 mmHg); mp 51—52 °C; Mass; *m/e*=149 (M^+). IR (liq. film); 3040, 2930, 1377 (C–H), 1010 cm^{-1} (C–O). PMR (CCl_4); δ: 1.34 (4H, C-10 and C-11 CH_2' s, m), 2.32 (4H, C-1, C-2, C-6, and C-7 CH's, m), 3.16 (2H, C-3 and C-5 CH's, m), 3.70 (2H, C-3 and C-5 CH's, m), 6.12 ppm (2H, C-8 and C-9 CH's, m). Found: C, 79.34; H, 9.32%. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39%.

General Procedures. 1,4-Naphthoquinone (1 mmol) and an olefin (2 mmol) were dissolved in dry benzene (25 ml) and irradiated in a glass tube with a high pressure Hg arc lamp (300 W) through a water layer 5 cm thick (10 °C). After the reaction was completed the photo-addition compounds were isolated by the usual work-up from the reaction mixture and subjected to further examination for structure determination.

*Identification of the Photo-addition Compounds. Bicyclo-[4.2.0]octano[2',3'-*h*]-5,8,13,14-tetraoxo-5,5a,6,7,7a,8,13,13a,13b,14-decahydropentaphene (3a)*: white needles, mp 235 °C. Found: C, 79.08; H, 5.35%. Calcd for $C_{28}H_{24}O_4$: C, 79.23; H, 5.70%. Mass: *m/e*=424 (M^+). IR (KBr disk): 1675 cm^{-1} (C=O). PMR ($CDCl_3$); δ 1.00—2.40 (12H, aliphatic protons, m), 3.43 (1H, C-7a CH, dd, J=6.0 and 11.0 Hz), 3.53 (1H, C-5a CH, dd, J=6.0 and 12.0 Hz), 4.50 (2H, C-13a and C-13 CH's, m), 7.85 (4H, aromatic protons, m), 8.16 ppm (4H, aromatic protons, m).

Bicyclo[2.2.1]heptano[2',3': 4,5]tricyclo[6.4.0.0^{3,6}]dodeca-8,10,12-triene-2,7-dione (1b): colorless cubes from *n*-hexane, mp 113.0—114.0 °C. Found: C, 81.15; H, 6.35%. Calcd for $C_{17}H_{16}O_2$: 80.92; H, 6.39%. Mass: *m/e*=252 (M^+). IR (KBr disk); 1670 cm^{-1} (C=O). PMR ($CDCl_3$): δ; 0.80—2.00 (8H, aliphatic protons, m), 2.40 (2H, C-4 and C-5 CH's, s), 3.18 (2H, C-3 and C-4 CH's, d, J=3.0 Hz), 7.80—8.30 ppm (4H, aromatic protons, m).

4-Oxo-1,4-dihydronaphthalene-1-spiro-*2'-bicyclo[2.2.1]heptano-[2'',3'': 3',4']oxetane (2b)*: colorless cubes from petroleum ether, mp 101.0—102.0 °C. Found: C, 80.76; H, 6.25. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39%. Mass; *m/e*=252 (M^+). IR (KBr disk); 1668 (C=O), 977 cm^{-1} (oxetane ring). UV max ($CHCl_3$); 248 nm (ε: 1.20×10^5), 281 (5.43×10^4). PMR (CCl_4): δ: 0.80—2.90 (9H, aliphatic protons, m), 5.05 (1H, C-3' CH, dd, J=5.0 and 6.0 Hz), 6.16 (1H, C-2 CH, d, J=10.0 Hz), 7.70 (1H, C-3 CH, d, J=10.0 Hz), 7.20—8.10 ppm (4H, aromatic protons, m).

*Bicyclo[2.2.1]heptano[2',3'-*h*]-5,8,13,14-tetraoxo-5,5a,6,7,7a,8,13,13a,13b,14-decahydropentaphene (3b)*: white needles from chloroform, mp 227.5—228.5 °C. Found: C, 78.84; H, 5.39. Calcd for $C_{27}H_{22}O_4$: C, 79.00; H, 5.40%. Mass *m/e*=410; (M^+). IR (KBr disk); 1670 cm^{-1} (C=O). UV max ($CHCl_3$): 256 nm (ε: 2.35×10^4), 304 (5.40×10^3). PMR ($CDCl_3$); δ: 0.60—1.70 (8H, aliphatic protons, m). 2.03 (2H, C-6 and C-7 CH's, m), 3.13 (1H, C-7a CH, dd, J=5.0 and 12.0 Hz), 3.27 (1H, C-5a CH, dd, J=5.0 and 14.0 Hz), 4.56 (2H, C-13a and C-13b CH's, d, J=5.0 Hz), 7.70—8.24 ppm (8H, aromatic protons, m).

Bicyclo[2.2.2]octano[2',3': 4,5]tricyclo[6.4.0.0^{3,6}]dodeca-8,10,12-triene-2,7-dione (1d): colorless cubes from benzene–petroleum ether, mp 141.5—142.3 °C. Found: C, 81.24; H, 6.76%. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%. Mass: *m/e*=266 (M^+). IR (KBr disk); 1674 cm^{-1} (C=O). UV max ($CHCl_3$); 254 nm (ε: 1.18×10^4), 302 (1.90×10^3), 309 (2.08×10^3), 348 (1.64×10^2). PMR ($CDCl_3$); δ: 1.40—2.30 (10H, aliphatic protons, m), 2.61 (2H, C-4 and C-5 CH's, broad s), 3.37 (2H,

C-3 and C-6 CH's, d, J=6.0 Hz), 7.70—8.30 ppm (4H, aromatic protons, m).

4-Oxo-1,4-dihydronaphthalene-1-spiro-*2'-bicyclo[2.2.2]octano[2'', 3'': 3',4']oxetane* (**2d**): assignment of the structure was confirmed by IR and UV spectra which were in good agreement with those of **2b**: IR (CCl_4 solution); 1670 (C=O), 980 cm^{-1} (oxetane ring). UV max ($CHCl_3$); 253, 281 nm.

Bicyclo[2.2.2]octano[2',3'-h]-*5,8,13,14-tetraoxo-5,5a,6,7,7a,8, 13,13a,13b,14-decahydropentaphene* (**3d**): white needles from benzene–petroleum ether, mp 245 °C (decomp.). Found: C, 79.15; H, 5.58%. Calcd for $C_{28}H_{24}O_4$: C, 79.21; H, 5.70%. Mass; m/e=424 (M^+). IR (KBr disk); 1675 cm^{-1} (C=O). UV max ($CHCl_3$); 258 nm (ε: 2.31×10^4), 300 (4.13×10^3), 308 (4.56×10^3). PMR ($CDCl_3$); δ: 1.35 (12H, aliphatic protons, m), 3.30 (2H, C-5a and C-7a CH's, m), 4.50 (2H, C-13a and C-13b CH's d, J=4.0 Hz), 7.77 (4H, aromatic protons, m), 8.08 ppm (4H, aromatic protons, m).

4-Oxo-1,4-dihydronaphthalene-1-spiro-*2'-3',3',4'-trimethyloxetane* (**9a**) *and 4-Oxo-1,4-dihydronaphthalene-1*-spiro-*2'-3',4',4'-trimethyloxetane* (**9b**): these two isomers were isolated as a mixture. The relative ratio of the isomer content (**9a**/**9b**) was estimated to be 1.3/1.0 through integration of the PMR signals due to the methine protons of the oxetane ring. They appeared at δ=4.74 ppm (C-4' CH, q, J=6.0 Hz) for **9a** and 2.86 ppm (C-3' CH, q, J=6.0 Hz) for **9b**, respectively; colorless oil. Mass; m/e=228 (M^+). IR (liq. film); 1670 (C=O), 960 cm^{-1} (oxetane ring).

Measurement of the Quantum Yields. Light of wavelengths in the range 300—400 nm (filters, Corning CS 7–54 and usual glass, 2 mm thick) was used. The quanta absorbed by the reaction mixture were calibrated using potassium ferrioxalate as a chemical actinometer.[18] The benzene solution of 1,4-naphthoquinone (0.100 M) and an olefin (0.200 M) in a quartz cell was degassed and subjected to measurement. After the reaction was over the reaction mixture was purified by thin layer chromatography on silica gel, the amount of photoaddition compounds produced being estimated by their absorptions in the UV region.

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