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Photocycloaddition Reaction of Alkyl-substituted 1,4-Naphthoquinones with Olefins. Substituent Effects on Controlling the Orientation of Cycloaddition Reaction

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Photolysis of a benzene solution of 2-alkyl- or 2,3-dialkyl-substituted 1,4-naphthoquinone mixed with an aryl-substituted ethylene afforded 3,4-benzobicyclo[4.2.0]octene-2,5-dione derivatives (cyclobutane type adducts) in a good yield without any other types of products. The orientation of the cycloaddition was likely to control by the adverse van der Waals repulsion of the substituents of the quinone and olefin in addition to the electronic effects of the substituents. The predominant factor orientating the cycloaddition seems to play the van der Waals repulsion due to the substituents both of quinone and olefin.

Photochemical reaction of 1,4-naphthoquinones with olefins have been investigated by several workers[1–3]. Especially the photoaddition reactions are of versatile possibilities, for it consists from one-step C–C or C–O bond formation reaction. The photo-addition products of quinone and olefins can be classified into the following three structural types; cyclobutane type adduct **A**, spiro-oxetane type adduct **B** *via* $2\pi+2\pi$ cycloaddition processes, and cyclohexane type adduct **C** *via* $2\pi+2\pi+2\pi$ cycloaddition process.

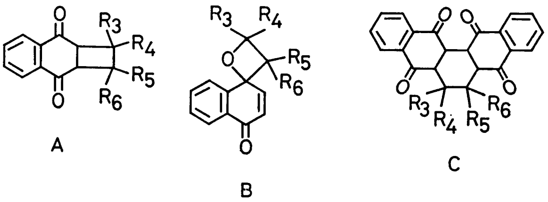


Fig. 1. The photo-addition products of 1,4-naphthoquinone and olefins.

The mechanism of the formation of type **C** products has been investigated in details by Maruyama, *et al.*[4]

Although photochemical reactions of substituted 1,4-naphthoquinones with some olefins have reported to yield cyclobutane type adducts **A**,[5,6] the systematic investigations in the fields have been sparse. In this paper, the present authors investigated the photochemical reactions of alkyl-substituted 1,4-naphthoquinones with aryl-substituted ethylenes and intended to clarify the substituent effects of quinones and olefins on the orientation of the photocycloaddition reaction.

Results and Discussion

Photocycloaddition Reaction of Alkyl-substituted 1,4-Naphthoquinones with Aryl-substituted Ethylenes. Irradiation of a solution of 2-methyl-1,4-naphthoquinone (**1a**) with styrene (**2a**) in benzene with the light through a Pyrex filter gave the mixture of three cycloaddition products in a high yield. The major product was isolated by thin layer chromatography (silica gel) and purified by recrystallization as white crystals. The structure was determined on the basis of spectroscopy (see Experimental) to be *anti*-1-methyl-8-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione(**3a**). The second product was obtained as a mixture with **3a**. The structure was assigned to *syn*-1-methyl-8-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione(**4a**) on the basis of spectral data. The third product was obtained as pure crystals which structure was assigned to *syn*-1-methyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione(**5a**).

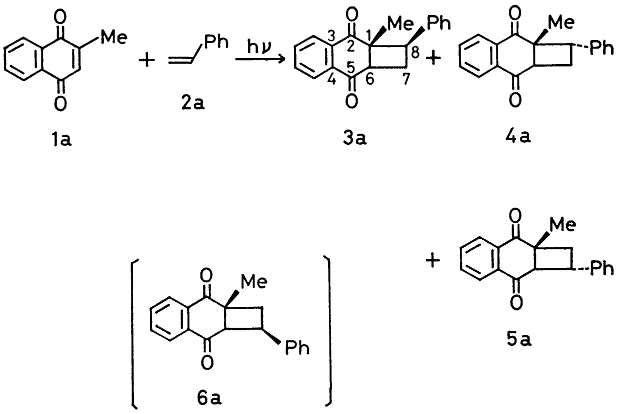


Fig. 2. Photochemical reaction of 2-methyl-1,4-naphthoquinone **1a** with styrene **2a**.

All of three products were cyclobutane type adducts *via* $2\pi+2\pi$ cycloaddition process. But, the corresponding *anti*-7-phenyl isomer expected(**6a**) was not detectable. These three products were unchanged by treatment with basic alumina, showing that the six-four ring fusion is cis.[8]

In a similar fashion, the photoreaction of 2-ethyl-1,4-naphthoquinone(**1b**) with styrene **2a** afforded three products **3b**, **4b**, and **5b**. No *anti*-7-phenyl isomer **6b** was obtained, too.

In these cases, the major products were the 8-phenyl isomers and the ratio of 7-phenyl isomer to 8-phenyl isomers was smaller for 2-methyl-1,4-naphthoquinone–styrene system, 1/6, than that for 2-ethyl-1,4-naphthoquinone–styrene system, 1/3.5.

The slow photo-induced isomerization between these two isomers (7-phenyl and 8-phenyl isomers) was realized, which was followed by means of NMR spectroscopy, but the rates of photo-isomerization were so slow that the distribution of the products was controlled kinetically.

The orientation of the addition could be affected

Table 1. Relative yields of photoproducts

Quinone	Olefin	Total yield %	7-Phenyl Anti(%)	 Syn(%)	8-Phenyl Anti(%)	 Syn(%)
1a	**2a**	80	(**6a**) 0	(**5a**) 15	(**3a**) 55	(**4a**) 30
1b	**2a**	73	(**6b**) 0	(**5b**) 24	(**3b**) 50	(**4b**) 26
1a	**2b**	95	(**6c**) 42	(**5c**) 10	(**3c**) 29	(**4c**) 19
1b	**2b**	95	(**6d**) 50	(**5d**) 14	(**3d**) 23	(**4d**) 13
1a	**2c**	73		(**5e**) 66	(**3e**) 34	
1b	**2c**	57		(**5f**) 80	(**3f**) 20	

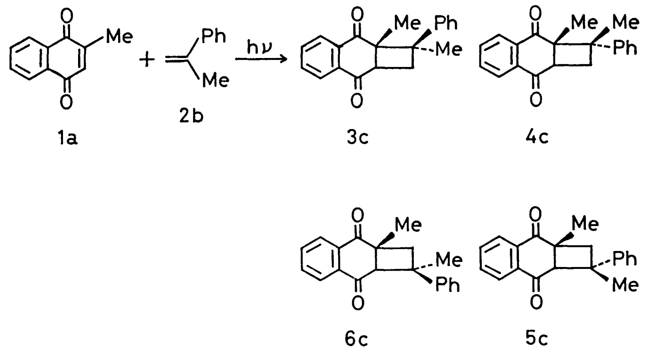


Fig. 3. Photochemical reaction of **1a** with 2-phenylpropene **2b**.

by both steric and electronic interactions between two substrates, 1,4-naphthoquinone and olefin. The results found in the 2-alkyl-1,4-naphthoquinone–styrene system indicate that the dipole-dipole interaction between the alkyl group on the quinone molecule and the phenyl group on styrene molecule presumably overcome the adverse van der Waals repulsion of these substituents.

The photocycloaddition of 2-methyl-1,4-naphthoquinone **1a** with 2-phenylpropene(**2b**) in bezene gave four cycloadducts. The major product (39%) was isolated as white crystals which structure was determined as *anti*-1,7-dimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]-octene-2,5-dione(**6c**). The second product (28%) was *anti*-1,8-dimethyl-8-phenyl-3,5-benzobicyclo[4.2.0]-octene-2,5-dione(**3c**).

The *syn*-7-phenyl (**5c**) (9%) and *syn*-8-phenyl isomer (**4c**) (18%) were obtained as the mixture, and the yields were determined by means of NMR spectroscopy. The ratio of 7-phenyl isomers to 8-phenyl isomers was about 1.

The photochemical reaction of 2-ethyl-1,4-naphthoquinone **1b** with 2-phenylpropene **2b** gave similarly two 8-phenyl derivatives (**3d**) and (**4d**), and two 7-phenyl derivatives (**5d**) and (**6d**). The major product (48%) was *anti*-ethyl-7-methyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**6d**). The *anti*-8-phenyl isomer was obtained in a yield of 22%. The syn isomers were obtained as a mixture. The ratio of 7-phenyl derivatives to 8-phenyl ones was about 1.5, which was larger than that of isomers in the case of **1a** and **2b**.

When 2-phenylpropene was employed as olefin, the methyl group on C-2 carbon of olefin would cancel out the dipole-dipole interaction caused by the phenyl group, and the adverse van der Waals repulsion of the substituent groups on the quinone and olefin may force to reverse the orientation of addition. Thus the ratio of 7-phenyl/8-phenyl adducts increased in accordance with the bulkiness of substituent groups, *i.e.* from hydrogen to methyl group. To support this conclusion, the photocycloadditions of 2-methyl- and 2-ethyl-1,4-naphthoquinone with 1,1-diphenylethylene (**2c**) were investigated under the same conditions.

A benzene solution containing 2-methyl-1,4-naphthoquinone **1a** and 1,1-diphenylethylene **2c** was irradiated through a Pyrex filter. The products were 1-methyl-7,7-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5e**) (48%) and 1-methyl-8,8-diphenyl-3,4-benzobicyclo-[4.2.0]octene-2,5-dione (**3e**) (25%). Similarly, 2-ethyl-1,4-naphthoquinone **1b** reacted photochemically with 1,1-diphenylethylene **2c** to give 1-ethyl-7,7-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5f**) (45%) as the major product and 1-ethyl-8,8-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3f**) (12%).

In these cases, the major product was the 7,7-diphenyl derivative and the ratio of 7,7-diphenyl/8,8-diphenyl isomer was 2 for 2-methyl-1,4-naphthoquinone–1,1-diphenylethylene system, and 4 for 2-ethyl-1,4-naphthoquinone–1,1-diphenylethylene system.

The results were illustrated in Table 1.

These results given in Table 1 indicated that the adverse van der Waals repulsion among the substituent groups in transition state could overcome sometimes the electronic attractive interaction caused by the substituents of reactants.

In the photoadducts of the quinone and 1,1-diphenylethylene, one of the two phenyl groups was situated above the quinone moiety from molecular model examination. The π-π interaction between quinone moiety and one of the two phenyl groups could be expected, but not with the other.

To substantiate the fact, the photocycloaddition of 2-methyl-1,4-naphthoquinone **1a** and 1,1-bis(*p*-methylphenyl)ethylene was carried out under the same irradiation conditions. The major product (46%) was 1-methyl-7,7-bis(*p*-methylphenyl)-3,4-benzobicyclo-[4.2.0]octene-2,5-dione (**5g**). The minor product was assigned the structure as 1-methyl-8,8-bis(*p*-methylphenyl)-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3g**) (28%).

The NMR spectra of these products showed that the signals due to two methyl groups on the two phenyls appeared at δ 2.0 and 2.3 ppm in chloroform-*d*, respectively. The phenyl protons appeared in the region

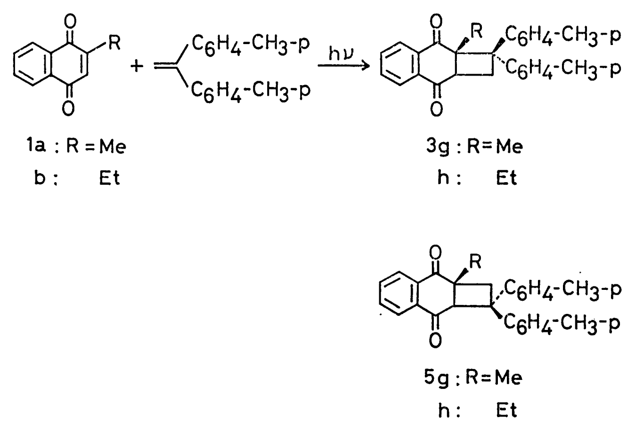


Fig. 4. Photochemical reaction of 2-alkyl-1,4-naphthoquinone with 1,1-bis(*p*-methylphenyl)ethylene.

of 6.9—7.1 and 7.2—7.3 ppm with two AB type quartets (see Experimental).

Analogous products, 1-ethyl-7,7-bis(*p*-methylphenyl)-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5h**) and 1-ethyl-8,8-bis(*p*-methylphenyl)-3,4-benzobicyclo[4.2.0]-octene-2,5-dione (**3h**) were obtained from the photoreaction of 2-ethyl-1,4-naphthoquinone **1b** with 1,1-bis(*p*-methylphenyl)ethylene.

The NMR spectra of both **3h** and **5h** also showed respectively two different *p*-methylphenyl signals. This fact clearly shows that between the one of two phenyl groups and quinone moiety the *π*-*π* interaction is operating.

The products ratio of two isomers, *i.e. anti* and *syn*, could reflect the steric or electronic courses of this type $2\pi+2\pi$ cycloaddition reaction. Further, the symmetrical 2,3-dialkyl-1,4-naphthoquinones were employed to investigate the substituent effects on the *anti*/*syn* isomers ratio of the products.

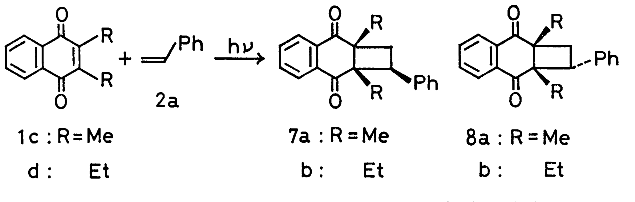


Fig. 5. Photochemical reaction of 2,3-dialkyl-1,4-naphthoquinone with styrene **2a**.

The photocycloaddition of 2,3-dimethyl-1,4-naphthoquinone (**1c**) with styrene **2a** gave *anti*-1,6-dimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7a**) in a yield of 84%, and the corresponding *syn* isomer (**8a**) in a yield of 16%.

The photoreaction of 2,3-diethyl-1,4-naphthoquinone (**1d**) with styrene **2a** gave *anti*-1,6-diethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7b**) in a yield of 93% and the *syn* isomer (**8b**) in a yield of 7%.

Table 2. Anti/syn ratio of photoproducts

Quinone	Olefin	7-Phenyl adducts	8-Phenyl adducts
1a	**2a**	0	1.88
1a	**2b**	4.20	1.56
1b	**2a**	0	2.00
1b	**2b**	3.69	1.69
1c	**2a**	5.25	
1c	**2b**	1.52	
1d	**2a**	13.33	
1d	**2b**	6.00	

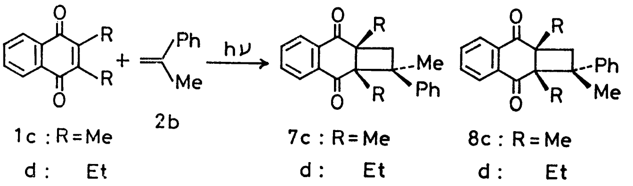


Fig. 6. Photochemical reaction of 2,3-dialkyl-1,4-naphthoquinone with 2-phenylpropene **2b**.

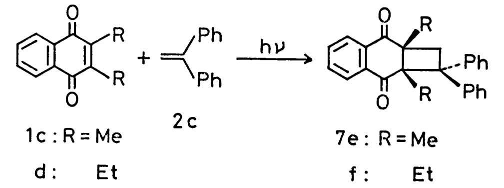


Fig. 7. Photochemical reaction of 2,3-dialkyl-1,4-naphthoquinone with 1,1-diphenylethylene **2c**.

The photoreaction of 2,3-dimethyl-1,4-naphthoquinone **1c** with 2-phenylpropene **2b** afforded two products, one of which was assigned as *anti*-1,6,7-trimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7c**)(38%) and the other was its *syn* isomer (**8c**) (20%). Similarly, the photocycloaddition of 2,3-diethyl-1,4-naphthoquinone **1d** and 2-phenylpropene **2b** gave *anti*-1,6-diethyl-7-methyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7d**) in a yield of 77% and the corresponding *syn* isomer (**8d**) in a yield of 13%.

The photocycloadditions of these symmetrical substituted 1,4-naphthoquinones(**1c** and **1d**) with 1,1-diphenylethylene **2c** gave 1,6-dialkyl-7,7-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7e** and **7f**) in high yields.

The results of the *anti*/*syn* ratio of photoproducts are given in Table 2.

The *anti*/*syn* ratio was larger than 1 with exception of the case of 7-phenyl derivatives obtained from 2-alkyl-1,4-naphthoquinone (**1a** and **1b**) and styrene **2a**. The ratio was reduced when the methyl group was introduced to C-1 carbon of styrene. The results found in these systems showed that the *anti* transition state was favored over the *syn* one, and that the adverse van der Waals repulsion of these substituents overcame the attractive force due to *π*-*π* overlap interaction between quinone moiety and phenyl group of olefin.

From the results it was shown that one of the major factors in determining the orientation of the photocycloaddition of alkyl-substituted 1,4-naphthoquinone and substituted styrene was the steric hinderance of the substituents of quinone and olefin.

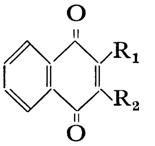
Determination of Quantum Yields. The quantum yields were determined by using potassium tris(oxalato)-ferrate(III) as the chemical actinometer.[9] The light from a 300 W high pressure mercury-arc lamp was

TABLE 3. QUANTUM YIELDS FOR QUINONE DISAPPEARANCE (Φ_d) AND THE PRODUCT FORMATION (Φ_p)

Quinone	Olefin	Φ_d	Relative Φ_d	Φ_p 7-Phenyl Anti	Φ_p 7-Phenyl Syn	Φ_p 8-Phenyl Anti	Φ_p 8-Phenyl Syn
1a	**2a**	0.82	1.00	0	0.10	0.44	0.24
1a	**2b**	0.66	0.81	0.26	0.03[a)]	0.18	0.12[a)]
1a	**2c**	0.60	0.73	0.38		0.20	
1b	**2a**	0.80	0.98	0	0.17	0.35[a)]	0.16[a)]
1b	**2b**	0.64	0.78	0.30	0.09[a)]	0.14	0.09[a)]
1b	**2c**	0.57	0.69	0.45		0.12	
1c	**2a**	0.65	0.79	0.53	0.12		
1c	**2b**	0.46	0.56	0.24	b)		
1c	**2c**	0.25	0.31	0.25			

a) The values were estimated by means of NMR spectroscopy. b) The values could not be determined.

TABLE 4. YIELDS AND PHYSICAL DATA OF QUINONES



	R_1	R_2	Yield/%[a)]	Mp/°C	nπ*(ε)	$\pi\pi$*(ε)
1a	Me	H	28	105.0—107.0	440 (50)	330 (2840)
1b	Et	H	29	89.5— 90.5	440 (70)	330 (2570)
1c	Me	Me	30	130.0—131.0	440 (60)	330 (2770)
1d	Et	Et	27	69.0— 69.5	440 (70)	330 (2330)

a) The values are isolated yields based on the amount of quinone used.

filtered through a potassium chromate–sodium carbonate solution[10)] (transmission: 300—330 nm).

Photochemical reactions for the determination were carried out holding the reaction at a low conversion to prevent an appreciable light absorption by the products. Quantum yields of the photochemical reactions measured in benzene solution were given in Table 3. Quantum yields for quinone disappearance were decreased in accordance with the larger steric repulsion of the substituent groups on quinone and olefin.

These results showed that the adverse van der Waals repulsion of substituent groups was playing an important role not only for controlling the orientation of the cycloaddition, but also for determining the rate of the reaction.

Reaction Mechanism. The absorption spectra of alkyl-substituted 1,4-naphthoquinones exhibited maxima (in chloroform) at 440 nm (ε: <100), 330 nm (ε: 2500—3000), and 245 nm(ε: *ca.* 15000). The lowest $\pi\pi$* absorption band of the quinones exhibited at 330 nm and nπ* absorption was almost masked by the long wavelength tail of the $\pi\pi$* band, and was apparently observed as a shoulder. When the photoreaction of 2-alkyl- or 2,3-dialkyl-1,4-naphthoquinone with olefins was undertaken by using the longer wavelength light than 400 nm, then none of photoadduct could be detected by means of NMR spectroscopy, and the quinone was recovered almost quantitatively.

The photocycloaddition of 2-methyl- **1a** or 2,3-dimethyl-1,4-naphthoquinone **1c** with 1,1-diphenylethylene **2c** was not quenched by addition of fluoranthene as a triplet quencher[12—14)] (E_T=54.2 kcal/mol) in the system. The present experimental results are likely to indicate the photocycloaddition between quinone and olefin proceeds *via* $\pi\pi$* singlet excited state of quinone, but to determine the true nature of the excited state responsible for the present cycloaddition reaction the further detailed mechanistic investigations should be done.

Experimental

The photolysis solution in a Pyrex test tube was irradiated externally with the light from a 300 W high pressure mercury-arc lamp (Eikosha, Halos PIH-300).

The melting points of photochemical products isolated were uncorrected.

The elemental analyses of photochemical products were performed at the Microanalysis Center of Kyoto University.

NMR spectra were observed with a JEOL PS-100 spectrometer at 100 MHz using TMS as the internal standard. Infrared spectra were observed with a JASCO IR-G spectrometer. Ultraviolet and visible spectra were observed with a Shimadzu UV-200 spectrometer,

The filter (Toshiba color glass filter VY-42) was employed for cutting the shorter wavelength light than 400 nm.

The 2-alkyl- and 2,3-dialkyl-1,4-naphthoquinones were prepared from 1,4-naphthoquinone and the corresponding carboxylic acid, acetic acid or propionic acid, according to the modification of Jacobsen and Torssell's method.[7)]

A solution containing 20 mmol of 1,4-naphthoquinone, 80 mmol of carboxylic acid and 0.5 g of silver nitrate in 40 ml of acetonitrile–water (50% v/v) was allowed to stir at 65 °C for the addition of 30 mmol of ammonium persulfate dissolved in 30 ml of water for 2 h. The mixture was allowed to stir for an additional 30 min. After neutralization with sodium carbonate, the solution was extracted with ether. The ethereal solution dried over magnesium sulfate was concentrated, and the crude residue was chromatographed through a silica-gel column using petroleum ether as the eluent. The yellow solid obtained was recrystallized from ethanol. The yields and physical data of alkyl-substituted 1,4-naphthoquinones were given in Table 4.

Styrene, 2-phenylpropene, and 1,1-diphenylethylene were purified by distillation under reduced pressure under nitrogen atomosphere. 1,1-Bis(*p*-methylphenyl)ethylene was prepared according to the method of Allen and Converese[15] from *p*-bromotoluene and *p*-methylacetophenone.

General procedure of photoreaction of alkyl-substituted 1,4-naphthoquinone with olefin was as follows. A solution containing 2 mmol of quinone and 4 mmol of olefin in 20 ml of benzene was irradiated in a Pyrex test tube for 12 to 24 h. After removal of the solvent under a reduced pressure, the residual yellow oil was separated by thin layer chromatography on silica gel.

Photolysis of 2-methyl-1,4-naphthoquinone **1a** with styrene **2a** afforded three products. The first product was *syn*-1-methyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5a**) in a yield of 11%. **5a**; white crystals, mp 94.0—95.0 °C; IR (KBr disk) 1670 cm^{-1}; UV (chloroform) $\lambda_{\max}$ 340 (ε:210), 308 (1540), 299 (1660), 254 (12000), and 244 nm (11100); NMR (CDCl$_3$) δ 1.68 (s, 3), 2.44 (dd, 1, J=8 and 10 Hz), 2.86 (dd, 1, J=8 and 10 Hz), 3.62 (d, 1, J=10 Hz), 4.24 (q, 1, J=10 Hz), 6.8—7.2 (m, 5), 7.4—7.7 (m, 3), and 7.9—8.1 ppm (m, 1); MS *m/e* 276 (M$^+$) and 104.

The second product was assigned the structure of *anti*-1-methyl-8-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3a**) (45%). **3a**; white crystals, mp 112.0—113.0 °C, IR (KBr disk) 1675 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 335 (ε:250), 308 (2170), 298 (2300), and 255 nm (12900); NMR (CDCl$_3$) δ 1.14 (s, 3), 2.40—2.70 (m, 1), 2.90—3.25 (m, 2), 3.80—4.04 (m, 1), 7.0—7.4 (m, 5), 7.70—7.90 (m, 2), and 8.0—8.24 ppm (m, 2); MS *m/e* 276 (M$^+$) and 104; EA: Found; C, 82.52; H, 6.02%; Calcd for $C_{19}H_{15}O_2$; C, 82.58; H, 5.84%.

The third component was obtained as a mixture with **3a** and assigned as *syn*-1-methyl-8-phenyl-3,4-benzobicyclo-[4.2.0]octene-2,5-dione (**4a**) on the basis of the NMR spectroscopy. **4a**; NMR (CDCl$_3$) δ 1.36 (s, 3), 2.1—2.4 (m, 1), 2.8—2.95 (m, 1), 3.4—3.6 (m, 2), 7.0—7.2 (m, 5), 7.6—7.8 (m, 2), and 7.9—8.1 ppm (m, 2); MS *m/e* 276 (M$^+$) and 104.

The NMR signal of methyl proton of **3a** appeared at the higher field due to the shielding effect of *cis*-phenyl group than that of **4a**, of which phenyl group was *trans* to the methyl group.

The photoadduct **3a** (50 mg) was stirred with basic alumina (3.0 g) in ether (30 ml) for 40 h at room temperature. The alumina was removed by filteration, and the filtrate was concentrated to give a light yellow solid (48 mg). The NMR analysis showed that there was no change during this treatment, confirming the *cis* four-six ring fusion in **3a**.

The photoadduct **3a** (30 mg) in benzene-d_6 (0.5 ml) in NMR tube was irradiated with a high pressure mercury-arc lamp for 12 h. The NMR spectrum of the material showed that the isomerization of **3a** to **4a** occurred by 5% at most.

When 2-ethyl-1,4-naphthoquinone **1b** with styrene **2a** was irradiated in benzene, three products were obtained. The first component was the mixture of *anti*- and *syn*-1-ethyl-8-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3b** and **4b**, respectively) (isomer ratio: 2:1) (total yield; 57%). The NMR spectrum of this component was very complex.[16]

The second component was obtained as white crystals. The structure was assigned *syn*-1-ethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5b**). **5b**; white crystals, mp 126.5—127.0 °C; IR (KBr disk) 1670 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 335 (ε:270), 308 (2200), 300 (2360), 253 (16600), and 242 nm (15600); NMR (CDCl$_3$) δ 0.94 (t, 3, J=8 Hz), 1.6—2.44 (m, 2), 2.54 (dd, 1, J=12 and 8 Hz), 2.82 (dd, 1, J=12 and 8 Hz), 3.72 (d, 1, J=10 Hz), 3.9—4.4 (m, 1), 6.8—7.3 (m, 5), 7.4—7.8 (m, 3), and 7.9—8.2 ppm (m, 1).

Photoreaction of **1a** and 2-phenylpropene **2b** afforded four addition products. The first product was obtained as white crystals in a yield of 39%. The structure was assigned as *anti*-1,7-dimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**6c**). **6c**; white crystals, mp 109.0—110.0 °C; IR (KBr disk) 1685 and 1675 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 335 (ε:200), 307 (1780), 298 (1880), and 256 nm (12900); NMR (CDCl$_3$) δ 1.12 (s, 3), 1.36 (s, 3), 2.69 (ABq, 2, J=26 and 16 Hz), 3.64 (s, 1), 7.0—7.44 (m, 5), 7.56—7.8 (m, 2), and 7.9—8.2 ppm (m, 2); EA; Found; C, 82.97; H, 6.17%; Calcd for $C_{20}H_{18}O_2$; C, 82.73; H, 6.25%.

The second product was assigned *anti*-1,8-dimethyl-8-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3c**). **3c**; white crystals mp 143.0—144.0 °C; IR (KBr disk) 1670 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 330 (ε:200), 307 (1710), 298 (1920), 254 (13000), and 242 nm (11200); NMR (CDCl$_3$) δ 1.20 (s, 6), 2.18 (d, 1, J=10 Hz), 2.88—3.24 (m, 2), 7.2—7.4 (m, 5), 7.6—7.8 (m, 2), and 7.96—8.2 ppm (m, 2); EA: Found; C, 82.88; H, 6.09%; Calcd for $C_{20}H_{18}O_2$; C, 82.73; H, 6.25%.

The third component was obtained as the mixture of two products. They were assigned *syn*-1,7-dimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5c**) and *syn*-1,8-dimethyl-8-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**4c**) (9 and 18%, respectively) on the basis of the NMR spectra. **5c**; NMR (CDCl$_3$) δ 1.52 (s, 3), 1.74 (s, 3), 2.22 (d, 1, J=12 Hz), 3.50 (s, 1), 6.8—7.2 (m, 5), 7.4—7.7 (m, 3), and 7.7—8.0 ppm (m, 1). **4c**; NMR (CDCl$_3$) δ 1.18 (s, 3), 1.24 (s, 3), 2.6—3.1 (m, 3), 6.8—7.3 (m, 5), 7.4—7.8 (m, 3), and 7.8—8.0 ppm (m, 1).

Irradiation of **1b** and **2b** afforded four cycloaddition products. The major product (48%) was assigned the structure of *anti*-1-ethyl-7-methyl-7-phenyl-3,4-benzobicyclo-[4.2.0]octene-2,5-dione (**6d**). **6d**; NMR (CDCl$_3$) δ 0.72 (t, 3, J=8 Hz), 1.20 (s, 3), 1.40—2.10 (dq, 2, J=8 and 8 Hz), 2.72 (ABq, 2, J=18 and 14 Hz), 3.80 (s, 1), 7.2—7.6 (m, 5), 7.7—8.0 (m, 2), and 8.1—8.4 ppm (m, 2).

The second product (22%) was obtained as white crystals, of which structure was assigned *anti*-1-ethyl-8-methyl-8-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**4d**). **4d**; white crystals, mp 137.0—138.0 °C; IR (KBr disk) 1675 and 1665 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 340 (ε:270), 308 (1770), 297 (2000), and 255 nm (13700); NMR (CDCl$_3$) δ 0.68 (t, 3, J=8 Hz), 0.8—1.4 (m, 1), 1.24 (s, 3), 1.8—2.2 (m, 1), 2.2—2.6 (m, 1), 3.0—3.4 (m, 2), 7.2—7.6 (m, 5), 7.7—8.0 (m, 2), and 8.1—8.4 ppm (m, 2); EA: Found; C, 82.98; H, 6.47%; Calcd for $C_{21}H_{20}O_2$; C, 82.86; H, 6.62%.

Photolysis of **1a** with 1,1-diphenylethylene **2c** gave two products. The first product (48%) was assigned the structure of 1-methyl-7,7-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5e**). **5e**; white crystals, mp 112.5—113.5 °C; IR (KBr disk) 1685 and 1670 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 310 (ε:1980), 302 (2080), 252 (12800), and 242 nm (13300); NMR (CDCl$_3$) 1.40 (s, 3), 2.58 (d, 1, J=12 Hz), 3.80 (d, 1, J=12 Hz), 4.16 (s, 1), 6.6—7.6 (m, 12), and 7.6—8.0 ppm (m, 2), MS *m/e* 352 (M$^+$) and 180; EA: Found; C, 85.50; H, 5.86%; Calcd for $C_{25}H_{20}O_2$; C, 85.20; H, 5.72%.

The second product (25%) was obtained as white crystals, assigned the structure 1-methyl-8,8-diphenyl-3,4-benzobicyclo-

[4.2.0]octene-2,5-dione (**3e**). **3e**; white crystals, mp 141.0—142.0 °C; IR (KBr disk) 1670 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 302 (ε:2050), 252 (13500), and 243 nm (13700); NMR (CDCl$_3$) δ 1.60 (s, 3), 3.14 (dd, 1, J=10 and 2 Hz), 3.42 (dd, 1, J=12 and 10 Hz), 3.74 (dd, 1, J=12 and 2Hz), 6.4—7.0 (m, 5), 7.0—7.6 (m, 7), and 7.7—8.0 ppm (m, 2), MS *m/e* 352 (M$^+$) and 180; EA: Found; C, 85.00; H, 5.59%; Calcd for $C_{25}H_{20}O_2$; C, 85.20; H, 5.72%.

Irradiation of **1b** with **2c** afforded two photoadducts. The first product (45%) was assigned the structure of 1-ethyl-7,7-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5f**). **5f**; white crystals, mp 135.0—136.0 °C; IR (KBr disk) 1665 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 310 (ε:1800), 302 (1890), 250 (11900), and 242 nm (12700); NMR (CDCl$_3$) δ 0.72 (t, 3, J=8 Hz), 1.50—2.30 (m, 2), 2.64 (d, 1, J=12 Hz), 3.84 (d, 1, J=12 Hz), 4.30 (s, 1), 6.6—7.6 (m, 12), and 7.7—8.0 ppm (m, 2); MS *m/e* 366 (M$^+$) and 180; EA: Found; C, 84.94; H, 6.16%; Calcd for $C_{26}H_{22}O_2$; C, 85.21; H, 6.05%.

The second product was assigned the structure of 1-ethyl-8,8-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3f**). **3f**; white crystals, mp 105.0—106.0 °C; IR (KBr disk) 1675 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 300 (ε:1800), 250 (13800), and 242 nm (14000); NMR (CDCl$_3$) δ 0.78 (t, 3, J=8 Hz), 1.38 (dq, 1, J=8 and 8 Hz), 2.76 (dq, 1, J=8 and 8 Hz), 3.1—3.7 (m, 3), 6.7—7.7 (m, 12), and 7.7—8.0 ppm (m, 2); MS *m/e* 366 (M$^+$) and 180; EA: Found; C, 85.10; H, 6.12%; Calcd for $C_{26}H_{22}O_2$; C, 85.21; H, 6.05%.

When **1a** was irradiated with 1,1-bis(*p*-methylphenyl)-ethylene, two products were obtained. The major product (46%) was assigned the structure of 1-methyl-7,7-bis(*p*-methylphenyl)-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5g**). **5g**; white crystals, mp 145.0—146.0 °C; NMR (CDCl$_3$) δ 1.44 (s, 3), 2.00 (s, 3), 2.32 (s, 3), 2.62 (d, 1, J=12 Hz), 3.84 (d, 1, J=12 Hz), 4.24 (s, 1), 6.82 (ABq, 4, J=18 and 8 Hz), 7.22 (ABq, 4, J=12 and 8 Hz), 7.4—7.6 (m, 2), and 7.7—8.0 ppm (m, 2); EA: Found; C, 85.35; H, 6.23%; Calcd for $C_{27}H_{24}O_2$; C, 85.23; H, 6.36%.

The minor product (28%) was obtained as white crystals, of which structure was assigned 1-methyl-8,8-bis(*p*-methylphenyl)-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3g**). **3g**; white crystals, mp 174.0—175.0 °C; NMR (CDCl$_3$) δ 1.60 (s, 3), 1.96 (s, 3), 2.28 (s, 3), 3.06 (dd, 1, J=10 and 2 Hz), 3.28 (t, 1, J=10 Hz), 3.62 (dd, 1, J=10 and 2 Hz), 6.66 (d, 2, J=8 Hz), 7.0—7.4 (m, 6), 7.4—7.6 (m, 2), and 7.8—8.0 ppm (m, 2); EA: Found; C, 85.01; H, 6.18%; Calcd for $C_{27}H_{24}O_2$; C, 85.23; H, 6.36%.

When **1b** and 1,1-bis(*p*-methylphenyl)ethylene were irradiated in benzene, two photoadducts were obtained. The major product (36%) was assigned the structure of 1-ethyl-7,7-bis(*p*-methylphenyl)-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**5h**). **5h**; white crystals, mp 125.0—126.0 °C; IR (KBr disk) 1670 cm^{-1}; NMR (CDCl$_3$) δ 0.68 (t, 3, J=8 Hz), 1.76 (dq, 2, J=30 and 8 Hz), 1.90 (s, 3), 2.20 (s, 3), 2.42 (d, 1, J=12 Hz), 3.58 (d, 1, J=12 Hz), 3.98 (s, 1), 6.52 (ABq, 4, J=24 and 8 Hz), 6.92 (ABq, 4, J=20 and 8 Hz), 7.16—7.40 (m, 2), and 7.48—7.7 ppm (m, 2), MS *m/e* 394 (M$^+$) and 208; EA: Found; C, 85.38; H, 6.64%; Calcd for $C_{28}H_{26}O_2$; C, 85.24; H, 6.64%.

The minor product (25%) was obtained as a light yellow viscous oil. The structure was assigned 1-ethyl-8,8-bis(*p*-methylphenyl)-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**3h**) on the basis of the NMR spectroscopy. **3h**; NMR (CDCl$_3$) δ 0.78 (t, 3, J=8 Hz), 1.10—1.50 (m, 1), 2.00 (s, 3), 2.30 (s, 3), 2.5—2.9 (m, 1), 3.1—3.7 (m, 3), 6.70 (d, 2, J=8 Hz), 7.0—7.4 (m, 6), and 7.5—7.6 ppm (m, 2), MS *m/e* 394 (M$^+$) and 208.

Photolysis of 2,3-dimethyl-1,4-naphthoquinone **1c** with styrene **2a** afforded two products. The major product (84%) was assigned the structure of *anti*-1,6-dimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7a**). **7a**; white crystals, mp 107.0—108.0 °C; IR (KBr disk) 1655 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 332 (ε:280), 306 (1900), 297 (2050), and 253 nm (13200); NMR (CDCl$_3$) δ 1.08 (s, 3), 1.12 (s, 3), 2.56 (d, 1, J=12 Hz), 2.58 (d, 1, J=12 Hz), 3.66 (dd, 1, J=12 and 8 Hz), 6.8—7.2 (m, 5), 7.6—7.8 (m, 2), and 8.0—8.2 ppm (m, 2); EA: Found; C, 82.86; H, 6.17%; Calcd for $C_{20}H_{18}O_2$; C, 82.73; H, 6.25%.

The minor product (16%) was assigned the structure of *syn*-1,6-dimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**8a**). **8a**; white crystals, mp 103.0—104.0 °C; IR (KBr disk) 1665 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 337 (δ:200), 305 (1450), 295 (1600), and 250 nm (10900); NMR (CDCl$_3$) δ 1.54 (s, 3), 1.60 (s, 3), 2.22 (dd, 1, J=12 and 8 Hz), 2.74 (dd, 1, J=12 and 10 Hz), 3.72 (dd, 1, J=10 and 8 Hz), 6.76—7.2 (m, 5), 7.4—7.6 (m, 3), and 7.84—8.04 ppm (m, 1); EA: Found; C, 82.74; H, 6.54%; Calcd for $C_{20}H_{18}O_2$; C, 82.73; H, 6.25%.

Irradiation of 2,3-diethyl-1,4-naphthoquinone (**1d**) with styrene **2a** gave two photoadducts. The major product (93%) was obtained as a light yellow viscous oil. The structure was assigned *anti*-1,6-diethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7b**) on the basis of the NMR spectrum. **7b**; NMR (CDCl$_3$) δ 0.78 (t, 3, J=8 Hz), 0.82 (t, 3, J=8 Hz), 1.4—2.1 (m, 4), 2.48 (dd, 1, J=12 and 10 Hz), 2.68 (dd, 1, J=12 and 8 Hz), 3.54 (dd, 1, J=10 and 8 Hz), 7.0—7.4 (m, 5), 7.5—7.8 (m, 2), and 7.9—8.2 ppm (m, 2).

The minor product (7%) was obtained as a yellow oil, of which structure was assigned *syn*-1,6-diethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**8b**) on the basis of the NMR spectroscopy. **8b**; NMR (CDCl$_3$) δ 0.56 (t, 3, J=8 Hz), 0.74 (t, 3, J=8 Hz), 1.2—2.8 (m, 5), 2.88 (dd, 1, J=12 and 8 Hz), 3.64 (dd, 1, J=10 and 8 Hz), 7.0—7.6 (m, 8), and 7.80 ppm (d, 1, 8 Hz).

Irradiation of **1c** with 2-phenylpropene **2b** afforded two products. The major product (38%) was obtained as white crystals. The structure was assigned *anti*-1,6,7-trimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7c**). **7c**; white crystals, mp 125.0—126.0 °C; IR (KBr disk) 1660 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 330 (ε:230), 296 (1880), and 254 nm (12900); NMR (CDCl$_3$) δ 1.12 (s, 3), 1.16 (s, 3), 1.26 (s, 3), 2.68 (s, 2), 7.0—7.4 (m, 5), 7.64—7.84 (m, 2), and 8.0—8.2 ppm (m, 2); EA: Found; C, 82.97; H, 6.53%; Calcd for $C_{21}H_{20}O_2$; C, 82.86; H, 6.62%.

The minor product (20%) was obtained as the mixture with **7c**. The former was assigned *syn*-1,6,7-trimethyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**8c**). **8c**; NMR (CDCl$_3$) δ 1.44 (s, 3), 1.52 (s, 3), 1.66 (s, 3), 2.16 (d, 1, J=14 Hz), 3.14 (d, 1, J=14 Hz), 6.8—7.2 (m, 5), 7.4—7.7 (m, 3), and 7.8—8.1 ppm (m, 1).

Photolysis of **1d** with **2b** gave two products. The major product (77%) was obtained as white crystals, of which structure was assigned *anti*-1,6-diethyl-7-methyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7d**). **7d**; white crystals, mp 162.0—163.0 °C; IR (KBr disk) 1670 cm^{-1}; UV (CHCl$_3$) $\lambda_{\max}$ 330 (ε:240), 295 (1610), and 250 nm (11400); NMR (CDCl$_3$) δ 0.72 (t, 3, J=8 Hz), 0.88 (t, 3, J=8 Hz), 1.18 (s, 3), 1.1—2.1 (m, 4), 2.64 (s, 2), 7.1—7.5 (m, 5), 7.64—7.9 (m, 2), and 7.9—8.1 ppm (m, 2); EA: Found; C, 83.17; H, 7.23%; Calcd for $C_{23}H_{24}O_2$; C, 83.10; H, 7.28%.

The minor product (13%) was obtained as the mixture with **7d**. The structure of the former was assigned *syn*-1,6-diethyl-7-methyl-7-phenyl-3,4-benzobicyclo[4.2.0]octene-

2,5-dione (**8d**) on the basis of the NMR spectroscopy. **8d**; NMR ($CDCl_3$) δ 0.72 (t, 3, J=8 Hz), 0.96 (t, 3, J=8 Hz), 1.52 (s, 3), 1.6—2.2 (m, 3), 2.20 (d, 1, J=12 Hz), 2.4—2.8 (m, 1), 3.30 (d, 1, J=12 Hz), and 7.3—8.0 ppm (m, 9).

Photolysis of **1c** with 1,1-diphenylethylene **2c** afforded a white crystalline product. The sptructure was assigned as 1,6-dimethyl-7,7-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7e**) in a yield of 87%. **7e**; white crystals, mp 170.0—171.0 °C; IR (KBr disk) 1675 and 1665 cm^{-1}; UV ($CHCl_3$) λ_{max} 302 (ε:2200), 254 (14000), and 243 nm (13600); NMR ($CDCl_3$) δ 1.24 (s, 3), 1.52 (s, 3), 2.80 (d, 1, J=12 Hz), 3.90 (d, 1, J=12 Hz), 6.60—7.0 (m, 4), 7.0—7.6 (m, 6), 7.74—7.9 (m, 1), and 7.96—8.1 ppm (m, 1), EA: Found; C, 85.09; H, 6.17%; Calcd for $C_{26}H_{22}O_2$; C, 85.21; H, 6.05%.

When **1e** was irradiated with **2c** in benzene, white crystals were obtained after purification by thick layer chromatography. The strucutre was assigned 1,6-diethyl-7,7-diphenyl-3,4-benzobicyclo[4.2.0]octene-2,5-dione (**7f**) in a yield of 92%. **7f**; white crystals, mp 180.0—181.0 °C; IR (KBr disk) 1685 and 1670 cm^{-1}; UV ($CHCl_3$) λ_{max} 300 (ε:2240), 252 (14200), and 243 nm (14100); NMR ($CDCl_3$) δ 0.80 (t, 3, J=8 Hz), 0.88 (t, 3, J=8 Hz), 1.32—2.08 (m, 3), 2.4—2.9 (m, 1), 2.80 (d, 1, J=12 Hz), 3.82 (d, 1, J=12 Hz), 6.6—7.84 (m, 13), and 7.96—8.12 ppm (m, 1), EA: Found; C, 85.39; H, 6.65%; Calcd for $C_{28}H_{26}O_2$; C, 85.24; H, 6.64%.

All measurements of quantum yields were made on a rotating assembly with a central light source (internal water-cooler mercury-arc lamp, Eikosha, Halos PIH-300). Samples in 15 mm Pyrex ampoules were placed in holders on the assembly placed at approximately 5 cm apart from the immersion well. The light was filtered by circulation of a solution containing 0.27 g of potassium chromate and 1.0 g of sodium carbonate in 1000 ml of distilled water. All studies were made at room temperature. After the irradiation, the degree of reaction was determined by means of quantitative ultraviolet absorption spectroscopy. The conversions in quinone quantities were run at highest to 15% or less. The mass balance in these runs was generally better than 90%.

Solutions of the quinone and the olefin in benzene containing excess amount of fluoranthene as a triplet quencher were irradiated under the conditions where more than 95% of the light was absorbed by the quinone. The reaction was monitored by TLC and in no case was the amount of products formed affected by addition of fluoranthene.

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