4,4-Diphenyl-1,3-dioxane (13). The same procedure as for 8 was used. Purification was obtained by HPLC on silica with CH_2Cl_2/CH_3CN (98.8/1.2), followed by recrystallization from petroleum ether, which afforded white needles: mp 91–92 °C; yield 42%; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.50 (2, t, 5-CH_2, $J_{H_5H_4}$ = 5.40 Hz), 3.96 (2, t, 4-CH_2, $J_{H_5H_4}$ = 5.40 Hz), 4.96 (2, s, OCH_2O), 7.35 (10, m, aryl H); ^{13}C NMR ($CDCl_3$) δ 35.52 (C-2), 63.79 (C-6), 79.37 (C-4), 89.20 (C-5); calcd for M^+, *m/e* 240.3012; found, *m/e* 240.3017.

1,1,3,3-Tetraphenyl-3-methoxypropanol (5). Monomethyl ether 5 was obtained by a Williamson ether synthesis in which the monosodium alkoxide of diol 4 was allowed to react with CH_3I in DMF during 10 h at room temperature. After purification by column chromatography on alumina with hexane/CH_2Cl_2 (80/20), followed by recrystallization from MeOH, white crystals were obtained: mp 100–101 °C; yield 82%; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.17 (3, s, OCH_3), 3.65 (2, s, 2-CH_2), 6.00 (1, s, OH), 7.35 (20, m, aryl H). Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.28; H, 6.60. Found: C, 85.56; H, 6.55.

1,1,3,3-Tetraphenyl-1,3-dimethoxypropane (15). Dimethyl ether 15 was obtained by a Williamson ether synthesis, in which the disodium alkoxide of diol 4 was allowed to react with CH_3I in THF during 8 h at room temperature. Chromatography on alumina with hexane/CH_2Cl_2 (90/10) followed by recrystallization from MeOH/CH_2Cl_2 (70/30) resulted in white crystals: mp 173–174 °C; yield 88%, ^1H NMR ($CDCl_3$, 60 MHz) δ 2.30 (6, s, OCH_3), 3.60 (2, s, 2-CH_2), 7.45 (20, m, aryl H). Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.29; H, 6.86. Found: C, 84.99; H, 6.91.

1,1,3-Triphenyl-1,3-dimethoxypropane (14). The same procedure as for 15 was used. A first purification was performed by column chromatography on alumina with hexane/CH_2Cl_2 (90/10), followed by recrystallization from EtOH/H_2O (95/15). Further purification was obtained by HPLC on silica with CH_2Cl_2/CH_3CN (98.8/1.2), which resulted in white crystals: mp 78–79 °C; yield 75%; ^1H NMR ($CDCl_3$, 360 MHz) δ 2.65 (1, dd, 2-CH_aH_b, $J_{H_{2a}H_{2b}}$ = −14.5 Hz, $J_{H_{2a}H_3}$ = 4 Hz), 2.90 (3, s, 3-OCH_3), 2.95 (3, s, 1-OCH_3), 3.00 (1, dd, 2-CH_aH_b, $J_{H_{2b}H_{2a}}$ = −14.5 Hz, $J_{H_{2b}H_3}$ = 6 Hz), 4.95 (1, dd, 3-CH, $J_{H_3H_{2a}}$ = 4 Hz, $J_{H_3H_{2b}}$ = 6 Hz), 7.30 (15, m, aryl H). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.13; H, 7.23. Found: C, 83.27; H, 7.31.

1-Methoxy-1-phenylethane (12). The same procedure as for 5 was used. Purification by preparative GLC (2 m, $^3/_8$ in. glass column, 10% Carbowax 20 M, 160 °C isothermal), followed by kugelröhr distillation at 0.1 mmHg, yielded a colorless oil yield 85%; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.47 (3, d, 2-CH_3, $J_{H_3H_1}$ = 6.7 Hz), 3.30 (3, s, OCH_3), 4.40 (1, q, 1-CH, $J_{H_1H_3}$ = 6.7 Hz), 7.50 (5, m, aryl H). Anal. Calcd for $C_9H_{12}O$: C, 79.41; H, 8.82. Found: C, 79.80; H, 8.79.

Acknowledgment. We are indebted to the N.F.W.O., the F.K.F.O., the University of Leuven Research Fund, the University Centre of Limburg, and the Ministry of Scientific Programming for financial support. Dr. Antheunis is acknowledged for supplying us with a sample of diol 11 and for the use of his NMR equipment.

Registry No. *meso*-1, 5381-86-2; (±)-2, 5355-61-3; 3, 14593-41-0; 4, 4705-01-5; 5, 87156-58-9; *cis*-6, 30630-83-2; *trans*-7, 87156-59-0; 8, 30693-18-6; 9, 87156-60-3; 10, 13961-05-2; 11, 93-56-1; 12, 4013-34-7; 13, 5702-27-2; 14, 87156-61-4; 15, 87156-62-5.

Nitrogen Effects in Photoreactions. Photochemistry of Iminoquinones with Olefins

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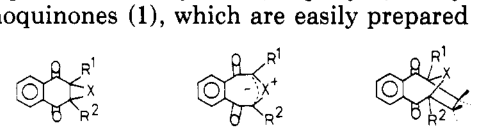
The photochemistry of epoxyquinones 1 and iminoquinones 2, which are electronic analogues, was investigated. Upon irradiation with olefins, they afforded cycloadducts 5 and 6, respectively. The order of relative reactivity (k_r/k_d) of the intermediate (3 or 4) with olefin was consistent with frontier orbital theory. The limiting quantum yields (ϕ_{max}) of 2 (~0.01) were about 50 times smaller than those of 1 (~0.5). Absorption and emission spectra revealed that 1 had a typical $n\pi^*$ lowest excited state and 2 had a rather large CT character. This difference of excited state character may be responsible for the differences in photochemical reactivity. Cycloadducts 5 from epoxyquinones 1 underwent further photorearrangement (ϕ ~ 0.1), whereas cycloadducts 6 were inert (ϕ < 10^{-4}) photochemically. Examination of the reason for the inertness of 6 revealed that the spatial location of the π system of the arylamino chromophore and that of the phthaloyl chromophore was very critical for the interaction between these two intramolecular chromophores and consequently for the photostability of adducts.

The photochemistry of 2,3-epoxy-2,3-dihydro-1,4-naphthoquinones (1), which are easily prepared by oxi-



1: X = O
2: X = NR
3: X = O
4: X = NR
5: X = O
6: X = NR

dation of the corresponding 1,4-naphthoquinones, has been studied extensively, and their photochemical behavior has been elucidated rather well.[1] Nonsubstituted or 2-alkyl substituted epoxyquinones undergo photoreactions characteristic of the carbonyl chromophore. They abstract hydrogen from hydrogen donors[1a] or form oxetanes with olefins.[1b] 2-Aryl or 2,3-disubstituted epoxyquinones, however, react as carbonyl ylides (3) or 1,3-diradicals via C–C bond cleavage of the oxirane ring. When olefins,[1b] carbonyl compounds,[1c] singlet oxygen,[1d] or alcohols were present, these epoxyquinones reacted with them to afford adducts that underwent further photorearrangements. The photochemistry of 2,3-imino-2,3-dihydro-1,4-naphthoquinones (2), which are electronically analogous to epoxyquinones 1, is also of interest but is quite unknown. As the result of our syntheses of compounds of type 2[2] we now report their photochemical reactions with olefins.

A. Padwa and his co-workers have studied the photochemistry of aziridinyl ketones and observed (a) photo-

(1) (a) Maruyama, K.; Arakawa, S. *J. Org. Chem.* **1977**, *42*, 3793. (b) Arakawa, S. *Ibid.* **1977**, *42*, 3800. (c) Maruyama, K.; Osuka, A. *Chem. Lett.* **1979**, 77. (d) Maruyama, K.; Osuka, A.; Suzuki, H. *J. Chem. Soc., Chem. Commun.* **1980**, 723. (e) Osuka, A.; Suzuki, H. *Chem. Lett.* **1981**, 201. (f) Maruyama, K.; Osuka, A.; Suzuki, H. *Ibid.* **1980**, 919.

(2) Maruyama, K.; Ogawa, T. *Chem. Lett.* **1981**, 1027.

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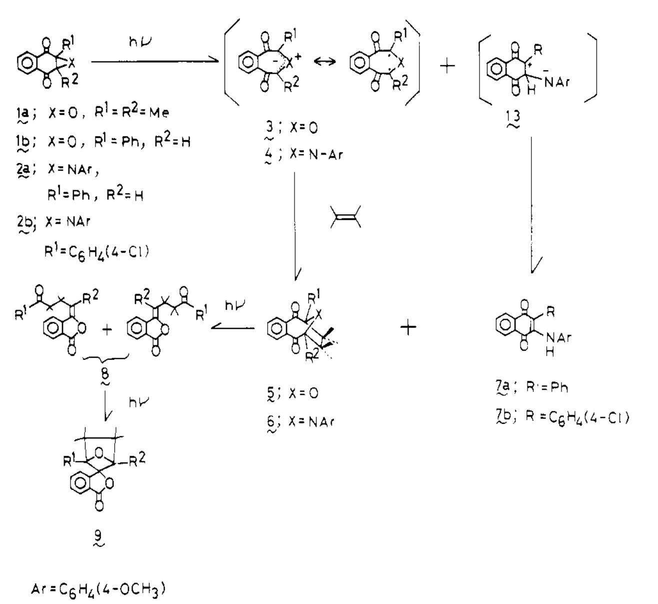


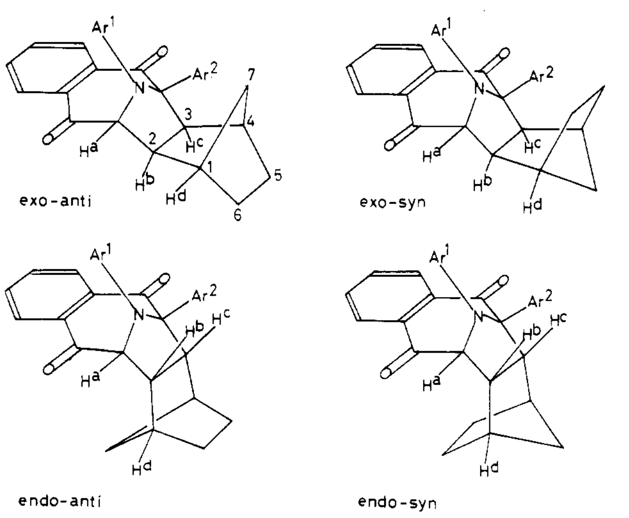
Figure 1. Photoreaction scheme.

deamination,[3a] (b) a photochemically induced 1,5-hydrogen shift,[3b] and (c) photochromism in rigid glasses at 77 K.[3c] However, the photoreaction of aziridinyl ketones with olefins was studied in a limited way only.[4] In this paper we report a great contrast between the photochemistry of iminoquinones 2 and epoxyquinones 1, which we ascribe to a "nitrogen effect".

Results and Discussion

Compounds of type 2 were made from 1,4-naphthoquinones and aryl azides.[2] However, because of synthetic difficulties only a few 2-aryl-2,3-(arylimino)-2,3-dihydro-1,4-naphthoquinones could be prepared successfully.

Photochemical Reactions with Simple Olefins. Irradiation of a benzene solution of 2-phenyl-2,3-((4-methoxyphenyl)imino)-2,3-dihydro-1,4-naphthoquinone **2a** and norbornene with a high-pressure Hg lamp through a Pyrex filter afforded a 1:1 adduct; i.e., 10,11-benzo-13-(4-methoxyphenyl)-1-phenyl-13-azatetracyclo[6.4.1.1^{3,6}.0^{2,7}]-tetradecene-9,12-dione (**6a**) in 60% and 3-((4-methoxyphenyl)amino)-2-phenyl-1,4-naphthoquinone (**7a**) in 5% yield (Figures 1 and 2). Similarly, 2-(4-chlorophenyl)-2,3-((4-methoxyphenyl)imino)-2,3-dihydro-1,4-naphthoquinone (**2b**) and norbornene afforded a 1:1 adduct **6b** (77%) and aminoquinone **7b** (20%) (Figure 3). The structure of the adduct was established as follows. The IR spectrum, which had a carbonyl band at 1685 cm^{-1}, and the ^{1}H NMR spectrum, characterized by the coupling pattern between H^a and H^b and the chemical shifts of H^b (δ 2.98) and H^c (δ 2.70), revealed that the adduct was not an oxetane but had one of the structures depicted. On the basis of the coupling constants between H^a and H^b (J = 10.38 Hz), and H^b and H^c (J = 9.77 Hz), and the lack of coupling between H^b and H^d it was reasonable to assign it the exo-anti configuration,[18] a conclusion also supported by experiments using Eu(fod)$_3$.[19]



6a: Ar^1= p-MeOC$_6$H$_4$, Ar^2=C$_6$H$_5$

6b: Ar^1= p-MeOC$_6$H$_4$, Ar^2=p-ClC$_6$H$_4$

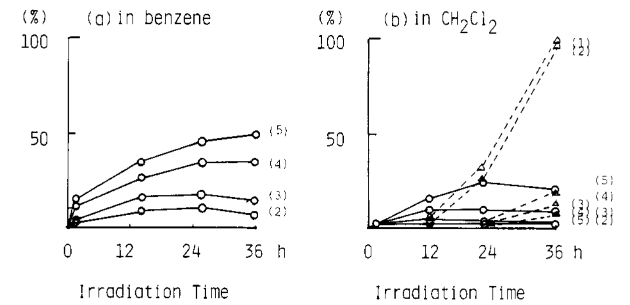


Figure 2. Time course for photoreaction of **2a** with norbornene: (1) 0 mM, (2) 20 mM, (3) 40 mM, (4) 80 mM, and (5) 160 mM norbornene and 5.6 mM iminoquinone **2a**; Δ, aminoquinone **7a**; O, cycloadduct **6a**.

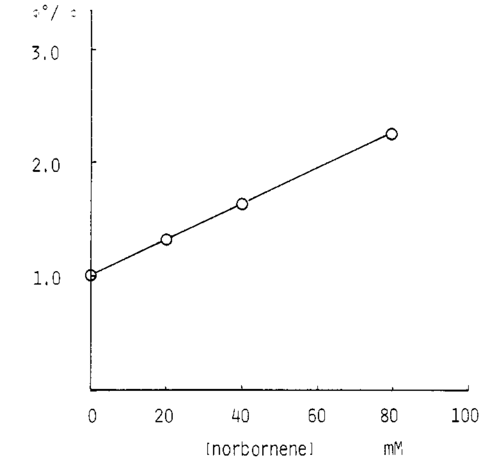


Figure 3. Quenching of aminoquinone formation by norbornene; quantum yield for aminoquinone formation.

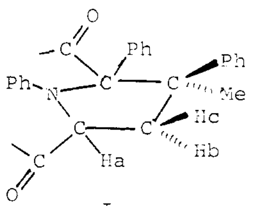
Irradiation of **2a** and norbornene in methanol or acetonitrile gave no cycloadduct but produced aminoquinone **7a** quantitatively, indicating that in a polar solvent heterolytic C–N bond cleavage occurred preferentially.

In reactions of **2** with other simple olefins such as 2-methylpropene, 2-methyl-2-butene, and 1-butene no cycloadducts were obtained, but only intractable complex mixtures which contained no cycloadduct as judged from the mass spectrum (Table I).

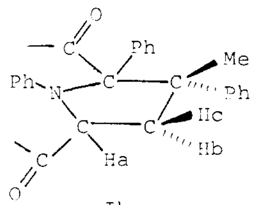
Photochemical Reactions with Conjugated Olefins. Irradiation of **2a** and α-methylstyrene in benzene afforded two isomeric cycloadducts **6f** (40%) and **6g** (40%). The values of the coupling constants between H^a and H^b (10 Hz for **6f** and 9 Hz for **6g**) and H^a and H^c (6 Hz for **6f** and 9 Hz for **6g**) indicated that the structures of **6f** and **6g** were compatible with either **Ia** or **Ib**, but not with **IIa** or **IIb**. 1,3-Pentadiene and **2a** also afforded cycloadducts **6e** in 95% yield.

(3) (a) Padwa, A.; Hamilton, L. *J. Am. Chem. Soc.* **1967**, *89*, 102. (b) Padwa, A.; Hamilton, L. *J. Heterocycl. Chem.* **1967**, *4*, 118. (c) Padwa, A.; Eisenhardt, W. *J. Am. Chem. Soc.* **1971**, *93*, 1400.

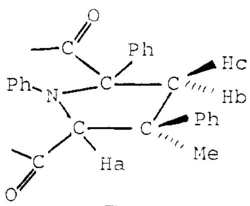
(4) Huisgen, R.; Mader, H. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 604.



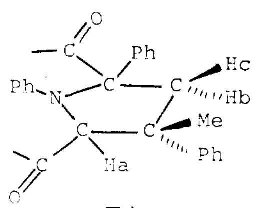
Ia



Ib



II a



II b

Photochemical Reactions with Electron Poor Olefins. Irradiation of a solution of **2a** and methyl acrylate afforded cycloadduct **6d** in 95% yield. The ^{1}H NMR spectrum that the carbomethoxyl group of the cycloadduct was situated close to the phenyl group, its chemical shift displaced by 0.4–0.6 ppm to higher field compared with the usual value (3.6–3.8 ppm). Hence the cycloadduct was endo.

Irradiation of **2a** and dimethyl maleate **10b** in benzene afforded cis cycloadduct **6j** in 70% yield, while the reaction with dimethyl fumarate **10a** produced cycloadducts **6h** and **6i** in the yields of 48% and 29%, respectively. The cycloaddition reaction, therefore, proceeds in the stereospecific manner, whereas S. Arakawa reported that photochemical reaction of **1a** with dimethyl maleate or with dimethyl fumarate afforded the same trans adduct **5a** in both cases.[1b] Because of these differences we reinvestigated the photochemical reaction of **1b** with **10a** and **10b**. Our results showed, however, that the photocycloaddition was completely stereospecific as shown in Table II. The discrepancy between our work and that of Arakawa could conceivably be due to isomerization of the cis to the trans isomer on prolonged irradiation, a hypothesis confirmed by the observation that isomerization from the cis to the trans isomer was facilitated by irradiation or by acid catalysis.

Photochemical Reactions with Electron Rich Olefins. Irradiation of **2a** with ethyl vinyl ether or 1,2-dichloroethylene afforded no cycloadducts.

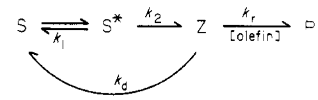
Reactivity. Scheme I is the most probable mechanism for this photoreaction. In the scheme, S is the starting iminoquinone or epoxyquinone, S* is excited S, Z is the intermediate 1,3-dipole (or 1,3-diradical), and P is the cycloadduct. Steady state analysis gives eq 1, indicating

$$\phi^{-1} = \phi_{max}^{-1}\ (1 + (k_d/k_r)[\mathrm{ol}]^{-1})$$
$$\phi_{max} = k_2/(k_1 + k_2) \qquad (1)$$

the influence of olefin concentration ([ol]) upon quantum yield of the cycloaddition (ϕ). In this equation ϕ_{max} is the quantum yield for formation of the intermediate Z from S*, and k_d/k_r indicates the relative reactivity of the intermediate for cycloaddition with olefins. These values can be evaluated by plotting the inverse of the olefin concentrations against the inverse of the quantum yields. A typical example is shown in Figure 4. Other results were tabulated in Table III.

(5) (a) Houk, K. N.; Sims, J.; Duke, Jr., R. E.; Strozier, R. W.; George J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287. (b) Houk, K. N.; Sims, J.; Watts, C. R.; Luskus, L. J. *Ibid.* **1973**, *95*, 7301.

Scheme I



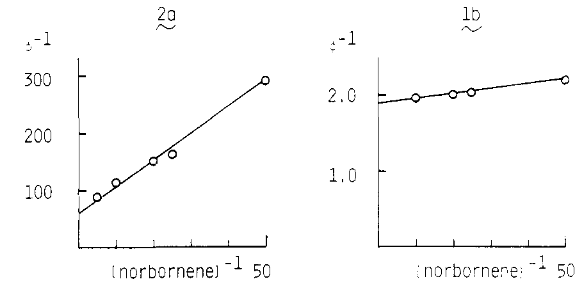


Figure 4. Dependence of cycloadduct yield of olefin concentration; ϕ, quantum yield for cycloaddition.

According to Scheme I, ϕ_{max} should be independent of the type of olefin used. However, the actual facts disagreed with this, the values of ϕ_{max} being dependent upon the olefin used. Presumably this is so because the excited S is quenched by olefins to some extent and the quenching rates are dependent upon the type of olefin used. In fact, in some cases quenching of the reaction by olefins apparently did occur as evidenced by the observation that the slope of the plot according to eq 1 showed a negative value at higher concentration (>200 mM) of olefin. In these cases ϕ_{max} and k_d/k_r were evaluated from the data obtained at lower concentration of olefin (<100 mM). This kind of quenching may be ascribed to exciplex formation between **2a** (or **1b**) and the olefins.[6] In general, excipex formation is favored when the energy gap between HOMOs of the interacting two molecules and that of the LUMOs is small.[7] If LUMO energy is considered as –EA (electron affinity) and the HOMO energy as –IP (ionization potential), in our experiments ionization potential gaps ($|\Delta IP|$) and electron affinity gaps ($|\Delta EA|$) between **2a** (or **1b**) and the olefins were plotted against ϕ_{max}, where the electron affinities of **2a** and **1b** were estimated as 1.08 eV for both compounds from charge transfer absorption of the complex with hydroquinone dimethyl ether as a donor in dichloromethane.[8] The ionization potential of **2a** and **1b** was estimated as 10.0 eV.[9] In fact good positive correlations were found between ϕ_{max} vs. $|\Delta EA|$ (correlation coefficient = 0.971) and ϕ_{max} vs. $|\Delta IP|$ (correlation coefficient = 0.831) in the case of 2a (Table IV). The other possible causes of quenching, e.g., triplet energy transfer, electron transfer, and chemical reactions, etc., could be excluded as discussed below. As shown in Table IV the triplet energies of the olefins used do not correlate with their ϕ_{max}; quenching via the triplet energy transfer is not as possible as quenching via electron transfer, because benzene, used as the solvent, is non-polar.[10]

On the average the value of ϕ_{max} of iminoquinone **2a** was much lower than that of epoxyquinone **1b** (ϕ_{max}(**1b**)/ϕ_{max}(**2a**) = 50). Why are iminoquinones so inefficient for the photoreaction? Iminoquinones emit only a weak

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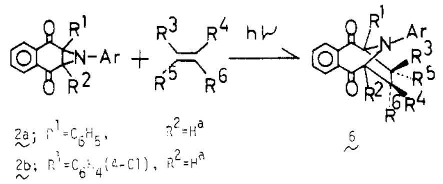
(7) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: London, 1976; p 209.
(8) (a) Peover, M. E. *Trans. Faraday. Soc.* **1962**, *58*, 1656. (b) Chatterjee, S. *J. Chem. Soc. B* **1971**, 2194.
(9) (a) Loutfy, R. O.; Loutfy, R. O. *J. Phys. Chem.* **1973**, *77*, 336. (b) Höger, G.; Meza, S.; Ruiz, M. E. *Acta Chem. Scand.* **1973**, *27*, 1860. (c) Kuhn, W. F.; Lewis, R. J.; Lilly, Jr., A. C. *J. Chem. Phys.* **1968**, *49*, 5550.
(10) Rehn, P.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

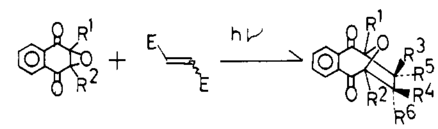
Table I. Photocycloaddition of Iminoquinone with Olefin[a]



iminoquinone	olefin	cycloadduct 6: compd	R³	R⁴	R⁵	R⁶	yield, %	note
2a[c]	norbornene[d]	**6a**	(norbornane ring)		H[c]	H[b]	60	g
2b[c]	norbornene[d]	**6b**	(norbornane ring)		H[c]	H[b]	77	h
2a[c]	acrylonitrile[d]	**6c**	H	H	CN	H	95	
2a[c]	methyl acrylate[d]	**6d**	H	H	E	H	95	
2a[c]	1,3-pentadiene[d]	**6e**	H	H	MeCH=CH	H	95	
2a[e]	α-methylstyrene[d]	**6f**	Me	H[b]	Ph	H[c]	40	
		6g	Ph	H[b]	Me	H[c]	40	
2a[e]	dimethyl fumarate (**10a**)	**6h**	E	H	H	E	48	i
		6i	H	E	E	H	29	
2a[e]	dimethyl maleate (**10b**)	**6j**	H	H	E	E	70	i
2b[e]	dimethyl maleate (**10b**)	**6k**	H	H	E	E	45	i

[a] Ar = C_6H_4 (4-OCH_3), E = CO_2CH_3. [b] Isolated yields. Conversion was 100%. [c] Ca. 17 mM. [d] Ca. 1 M. [e] Ca. 3 mM. [f] Ca. 70 mM. [g] 5% of aminoquinone **3a** was produced. [h] 20% of aminoquinone was produced. [i] Recovered olefin retained the stereochemistry.

Table II. Stereochemistry for Photocycloaddition of Epoxyquinone with Olefin[a]



epoxyquinone[b]	olefin[c]	cycloadduct 5	R³	R⁴	R⁵	R⁶	conversion, %	yield, %	note
1a	dimethyl fumarate	**5a**	E	H	H	E	36	70	d
1a	dimethyl maleate	**5a**	E	H	H	E	42	33	e
		5b	H	H	E	E		43	f
1b	dimethyl fumarate	**5c**	E	H	H	E	68	32	e
			H	E	E	H			
1b	dimethyl maleate	**5d**	H	H	E	E	17	100	e

[a] E = CO_2CH_3. [b] Ca. 20 mM. [c] Ca. 35 mM. [d] Recovered olefin was isomerized to dimethyl maleate. [e] Recovered olefin retained the stereochemistry. [f] Concomitant with **5a**.

Table III. Limiting Quantum Yields and Relative Reactivity

olefin	2a: ϕ_{50} mM	2a: ϕ_{max}	2a: k_r/k_d	1b: ϕ_{50} mM	1b: ϕ_{max}	1b: k_r/k_d
norbornene	0.006_6	0.01_8	12	0.4_8	0.5_3	300
dimethyl fumarate	0.007_8	0.008_5	>1000	0.5_0	0.5_2	180
1,3-pentadiene	0.005_1	0.005_8	120	0.4_5	0.6_3	80
methyl acrylate	0.005_1	0.005_0	>1000	0.5_9	0.5_9	>1000
acrylonitrile	0.007_5	0.007_5	>1000	0.5_8	0.5_8	>1000
α-methylstyrene	0.002_8	0.02_1	4	0.4_7	0.5_2	140

structureless phosphorescence at 77 K which is not observable at room temperature (Figure 5). The UV absorption spectra of iminoquinones show little solvent dependence and a large dependence on the arylamino substituent (Tables V and VI). This makes it probable that the excited state of iminoquinone loses its nπ* and has ππ* or CT character, compared with epoxyquinone, due to the electronic interaction between the phthaloyl chromophore and aryl amino chromophore. In contrast with iminoquinone **2a**, epoxyquinone **1b** emitted an intense phosphorescence at 77 K which can be attributed to emission from the nπ* level (Figure 5), and emission was also observed at room temperature. In polar solvents the UV spectra of the epoxyquinones showed a blue shift relative to those in nonpolar solvents (Table VII). From these facts the lowest excited state of epoxyquinones may be assigned to a typical nπ* state. Since ring opening of azirizinyl ketones or epoxyketones can be regarded as β-fission of the carbonyl nπ* state, it is reasonable to conclude that an excited state with large nπ* character such as that of the epoxyquinones undergoes β-fission more efficiently than an excited state with smaller nπ* character such as that of the iminoquinones. The excitation energy of iminoquinones might be released thermally via electron

Table IV. Physical Properties of the Olefins

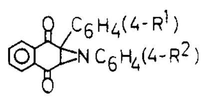
	IP,[a] eV	|ΔIP|	EA,[a] eV	|ΔEA|	E_S[b]	E_T[b]
norbornene	8.97	1.03				74
dimethyl fumarate	10.5[e]	0.5	0.6	0.48		
1,3-pentadiene					90	59
methyl acrylate	10.72	0.72	0.8	0.28	(74)[c]	(70)[c]
acrylonitrile	10.91	0.91	1.2	0.12	(74)[c]	(70)[c]
α-methylstyrene	(8.48)[d]	1.52	(−0.55)[d]	1.63	(98.2)[d]	(61.7)[d]
correlation coefficients[f]		0.831		0.971	0.756	0.049

[a] See ref 5. [b] Given in kcal/mol. Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; pp 3-21. [c] Data for acrolein. [d] Data for styrene. [e] Kobayashi, T.; Yokota, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 412. [f] Correlation coefficients with ϕ_{max} of **2a**.

Table V. Solvent Dependency of the UV Absorption Spectra of Imino- and Epoxyquinone

	λ_{max} (ϵ_{max})		
compd	C_6H_6	CH_3CN	EPA
2a	360 (600) sh	360 (600) sh	356 (680) sh
	311 (3000) sh	310 (2600) sh	310 (3100) sh
	295 (4000) sh	290 (3600) sh	
		233 (76 000)	
1b	348 (350) sh	340 (280) sh	336 (400) sh
	308 (3000)	305 (2000)	304 (3000)
		262 (4800)	
		231 (28 000)	

Table VI. Substituent Dependency of the UV Absorption Spectra of Iminoquinone



R^1	R^2	lowest absorption band λ_{max}, nm (ϵ_{max})
H	Cl	353 (540)
H	H	355 (510)
H	Br	352 (590)
Cl	Cl	353 (540)
Cl	OCH_3	360 (710)
H	OCH_3	360 (600)
OCH_3	OCH_3	360 (750)

Table VII. Spectroscopic Properties of Imino- and Epoxyquinone

	solvent	2a	1b
lowest energy absorption band λ_{max}, nm (ϵ_{max})	C_6H_6	360 (600)	348 (350)
	CH_3CN	360 (600)	341 (280)
fluorescence λ_{max}, nm	CH_3CN	380	365
phosphorescence 0-0 band, nm[a]	EPA	~410	415
life time, ms[a]	EPA	1.8	9.7

[a] Measured at 77 K.

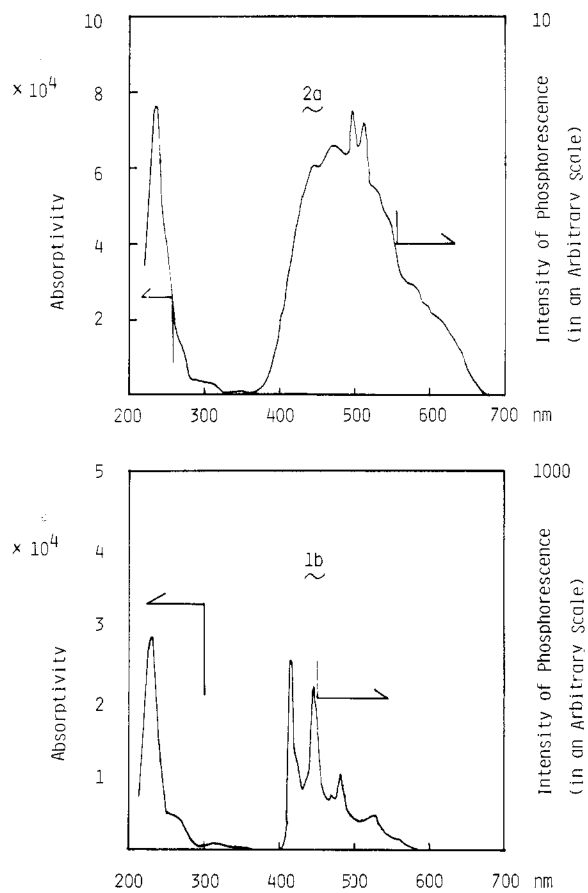


Figure 5. UV absorption and phosphorescence spectra.

transfer between the phthaloyl and arylamino chromophores.

Olefins which reacted with iminoquinones relatively efficiently were conjugated olefins (abbreviated as C-olefins) such as α-methylstyrene and piperylene and electron-deficient olefins (abbreviated as Z-olefins) such as acrylonitrile, methylacrylate, dimethyl maleate, and dimethyl fumarate. Alkyl substituted olefins (abbreviated as R-olefins) and electron rich olefins (abbreviated as X-olefins) were less reactive. Frontier orbital theory can explain this difference if we assume that azomethine ylide **4** generated photochemically add to olefins in a concerted manner. Relative energies of the frontier orbitals are as follows:[5] A C-olefin has higher HOMO and lower LUMO energies, a Z-olefin has lower HOMO and lower LUMO energies, and an X-olefin has higher HOMO and higher LUMO energies. Lower LUMO energies are common to the reactive C-olefin and Z-olefin. Accordingly, differences in the reactivity of an olefin in the photoreaction with **2a** can be understood if we assume that azomethine ylides **4** have relatively high HOMO energies and that the interaction between the HOMO of **4** and the LUMO of olefins is most favorable since it is dipole HOMO controlled.

Epoxyquinone **1a** afforded cycloadducts not only with C-olefins or Z-olefins but also with X-olefins.[1f] Two possible explanations for this are: (1) the HOMO energy of carbonyl ylide **3** derived from photoexcited **1b** is higher than that of azomethine ylide **4** and begins to interact with the LUMO of the X-olefin, or (2) the LUMO of **3** is of lower energies than that of **4** and interacts with the HOMO of the X-olefin. Calculations for the simplest system according to K. N. Houk and co-workers[5] showed that the HOMO energies of the carbonyl ylide and the azomethine ylide were similar (ca. -7 eV). However, the LUMO of the carbonyl ylide was ca. -3 eV and that of the azomethine ylide was ca. -4 eV. Because the LUMO energies of the carbonyl ylide are lower, the second explanation is more reasonable.

In order to find optimum conditions for the photocycloaddition, the olefin concentration was varied in several solvents, and product formation was followed at intervals. As described previously, in methanol or acetonitrile no cycloadduct was produced but aminoquinone **7a** was formed exclusively. Figure 2 shows the results obtained in methylene chloride and in benzene. In both solvents the yield of the cycloadduct **6a** showed a plateau at a time which depended on the olefin concentration. After that time further irradiation did not increase the yield of cycloadduct even though considerable amounts of substrate remained in the solution. Therefore, high olefin concentration was essential to obtain the cycloadduct in good yield. In methylene chloride, aminoquinone formation competed with cycloaddition. The rate of formation of **7a** increased with prolonged irradiation. This might be because some acidic species were produced photochemically and catalyzed the isomerization of **2a** to **7a**. Higher concentrations of olefin seemed to quench aminoquinone formation. In order to exclude alteration of solvent polarity caused by increasing amounts of olefin as a factor, four samples containing **2a**, norbornene, and norbornane were prepared in such a concentration that the total amounts of norbornene and norbornane were kept constant. These were irradiated in a merry-go-round apparatus and the amounts of **7a** were determined by HPLC. As shown in Figure 3 norbornene clearly quenched aminoquinone formation. The Stern-Volmer constant was about 30. Thus, **7a** may be produced by two pathways; that is, via acid-catalyzed and via photochemically-excited pathways. **7a** formation could be quenched by exciplex formation of excited **2a** with norbornene. Ionic intermediates such as **13** (Figure 1) may be responsible for aminoquinone formation via photochemically-excited pathways, since the more polar the solvent used the more efficiently aminoquinone was produced.

Photostabilities of the Cycloadducts. In general, the cycloadducts **5** from epoxyquinones easily underwent secondary photoinduced isomerization initiated by α-cleavage. On the other hand, the cycloadducts **6** from iminoquinones were inert photochemically. This remarkable difference may be caused by intramolecular electron transfer in **6** from the amino chromophore to the phthaloyl chromophore, by which process the excited state of **6** could be quenched. In order to investigate this possibility, we studied the quenching of **5e** by *N,N*-dimethylaniline (**11**). We may regard **5e** as a model for the phthaloyl chromophore of **6**, and **11** as an aryl amino chromophore. Upon irradiation **5** isomerized to **8**.[1b] Benzene solutions of various concentrations of **11** and **5** were irradiated at 313 or 366 nm for 1 h in a merry-go-round apparatus and the amounts of **5** and **8** were determined by means of HPLC. The results are depicted in Figure 6.

When the concentration of **11** is higher than 20 mM **11** will absorb more than 95% of 313 nm light and **5** (1 mM) less than 5% from the absorption coefficients of **5** and **11** at 313 nm. Even then **5** isomerized to **8** in good yield as shown in Figure 6. Especially in the case of **5e** the apparent quantum yield increased when **11** was present (Figure 6a). Thus, it is concluded that **11** sensitizes pho-

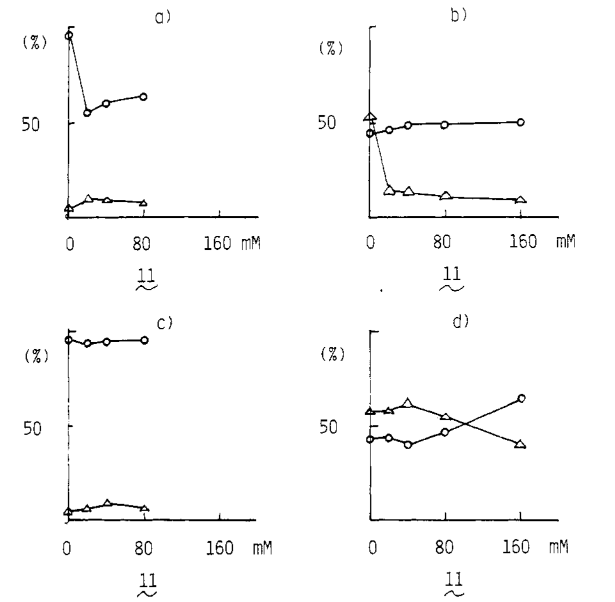


Figure 6. Effect of *N,N*-dimethylaniline **11** on the photoisomerism of **5** to **8**; adduct **5**; isomerized product **8**. Excitation of **11**: (a) irradiation of **5e** by 313 nm light and (b) irradiation of **5c** by 313 nm light. Excitation of **5**: (c) irradiation of **5e** by 366 nm light and (d) Irradiation of **5c** by 366 nm light.

Table VIII. Quantum Yields for Disappearance of Adducts

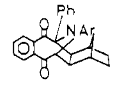
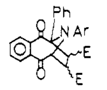
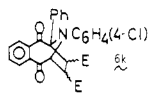
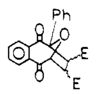
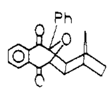
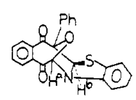
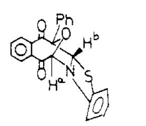
adducts	ϕ_{dis}
5c (1b + dimethyl fumarate)	0.12 ± 0.005
5e (1b + norbornene)	0.07 ± 0.02
12a (1b + benzthiazole, exo)	0.024 ± 0.006
12b (1b + benzthiazole, endo)	0.012 ± 0.008
6h + 6i (2a + dimethyl fumarate)	$<10^{-4}$
6a (2a + norbornene)	$<10^{-4}$

toisomerization of **5**. At 366 nm **5** absorbs more than 99% of the energy and under these conditions addition of **11** did not affect the quantum yield of the isomerization of **5** (Figure 6c,d). Similarly, in acetonitrile, isomerization of **5** was not quenched by **11**. Accordingly, the aryl amino chromophore does not quench the phthaloyl chromophore if the two chromophores are separated electronically. Therefore, it is reasonable to think that intramolecular interaction between the aryl amino and phthaloyl chromophores produced a new chromophore which is inert on further irradiation.

To investigate the effect of an aryl amino group within the same molecule on the photochemical α-cleavage reaction of the phthaloyl moiety, we prepared photoadducts of epoxyquinone **1b** with benzthiazole and studied their UV spectra and photoreactivity.

Irradiation in benzene of epoxyquinone **1b** and benzthiazole for 40 h afforded an exo adduct **12a** and an endo adduct **12b**. The structure assignment was based on the observation that H^b of **12a** at δ 6.50 was downfield to H^b of **12b** at δ 5.96. This can be attributed to the deshielding effect of the benzene ring of the phthaloyl group in an exo adduct. The quantum yields for the disappearance of adducts (ca. 4×10^{-4} M solutions in benzene) are tabulated in Table VIII. If as in **6** or **12** the adducts contain an aryl amino chromophore, the quantum yields for disappearance were lower than those for molecules such as **5c** or **5e** in which the aryl amino chromophore was absent. Even though the adducts from iminoquinone were irradiated by $1-5 \times 10^{-4}$ photons, no change was detected within experimental error ($\pm 1 \times 10^{-8}$ mol). However, in the case

Table IX. Spectroscopic Properties of Cycloadducts in Different Solvents

compd	UV absorption bands λ_{max}, nm (ϵ_{max})			fluorescence λ_{max}
	CH_3CN	CH_3OH	C_6H_6	CH_3CN
 6a	440 (160) 366 (320) sh 355 (330) sh 298 (3600) 246 (20 000)	440 (90) 366 (270) sh 355 (290) sh 298 (2200) 246 (12 000)	440 (110) 370 (310) sh 356 (360) sh 302 (4200)	390
 6h	441 (150) 356 (310) sh 303 (4000) 230 (27 000)	440 (100) 352 (290) sh 301 (3700)	450)150) 356 (310) sh 306 (4800)	350
 6k	412 (150) 349 (350) 301 (3700) 254 (23 000) 232 (27 000)		419 (160) 352 (440) 303 (4500)	350
 5c	331 (660) 295 (1300) 248 (8800) 227 (23 000)		328 (830) 297 (1900)	360
 5e	335 (550) 293 (1200) 245 (10 000) sh 228 (20 000)	334 (550) 294 (1200) 245 (10 000) sh 228 (20 000)	342 (600) 298 (1400)	370
 12a		330 (840) sh 299 (2600) 228 (26 000)	336 (800) sh 298 (3600)	
 12b		385 (330) sh 344 (880) sh 297 (4300) 227 (39 000)	387 (340) sh 344 (880) sh 300 (4200)	

of **12a** or **12b** suppression of the photoisomerization was not as pronounced as in the cases of **6h**, **6i**, or **6a**.

The UV spectra of the adducts (Table IX) support the view that the phthaloyl chromophore interacts intramolecularly with the aryl amino chromophore. When **6** or **12** bear an aryl amino chromophore they have a new absorption band in the region of 350–450 nm, which is absent in the case of **5c** or **5e**. That of **6** appeared in the region of the shortest wavelength and showed the strongest intensity. That of **12b** (endo) had intermediate intensity and wavelength, whereas that of **12a** (exo) was little different from those of adducts with no aryl amino chromophore. Intensity and wavelength of the new absorption bands are presumably an indication of the degree of interaction between the phthaloyl and aryl amino chromophores, which is then in the order **6** > **12b** > **12a** > **5**. This order parallels the order of quantum yields for the disappearance of the adducts. Therefore the interaction between aryl amino and phthaloyl chromophores is undoubtedly responsible for suppressing photochemical isomerization of the adducts.

Since the degree of interaction is larger in **12b** (endo) than in **12a** (exo), it is probably a through space interaction of the two aryl π-systems. That is, in the endo isomer the π-systems of phthaloyl and that of aryl amino are very close and the interaction between them is stronger than that in the exo isomer in which the two aryl π-systems are far apart. For the same reason, the interaction in **6** is stronger than in **12**. In **6**, the two aryl π-systems can overlap each other almost completely, whereas in **12b** the two aryl π-systems deviate a little from each other.

Since the wavelength of the lowest band shifted towards shorter wavelength in **6** when the para substituent on the aryl amino group was changed from methoxy to chloro, the lowest band due to the interaction mentioned above probably has a CT character. Since the electronic state of CT is inert in photochemical isomerizations of this type, the reactivity should diminish more as the interaction becomes stronger.[16]

Several investigators have reported on the photochemistry of ketones bearing amino chromophores in the same molecules.[11-13] However, an interaction of amino and carbonyl chromophores in the ground state as strong as that in **6** has not been observed previously, even in the case of α-amino ketones. Wagner and co-workers have claimed that overlap of the nitrogen lone pair orbital with the carbonyl n orbital is significant for intramolecular CT quenching.[12] Verhoeven and co-workers have found that through bond interaction between two n electron systems A and B may be expected when the lone pair orbitals on A and B are parallel to each other.[15] In the case of **6** and

(11) (a) Wald, G. *Nature (London)*, **1968**, *216*, 800. (b) Cohen, S. G.; Chao, H. M. *J. Am. Chem. Soc.* **1968**, *90*, 165. (c) Cohen, S. G.; Baumgarten, R. J. *Ibid.* **1967**, *89*, 3471.

(12) (a) Wagner, P. J.; Scheve, B. J. *J. Am. Chem. Soc.* **1977**, *99*, 1858. (b) Wagner, P. J.; Ersfeld, D. A. *Ibid.* **1976**, *98*, 4515. (c) Wagner, P. J.; Kemppainen, A. E.; Tellinek, T. *Ibid.* **1972**, *94*, 7512.

(13) Halpern, A. M.; Lyons, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 3242.

(14) The quantity of **8c** diminished when **11** was added. However intramolecular oxetane type compound **9** was not formed. Compound **8c** seemed to react with **11** and afforded a gum.

(15) Dekkers, A. W. J.; Verhoeven, J. W.; Speckamp, W. N. *Tetrahedron* **1973**, *29*, 1691.

(16) (a) Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664. (b) Cohen, S. G.; Cohen, J. I. *J. Phys. Chem.* **1968**, *72*, 3782. (c) Brown, R. G.; Porter, G. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1569. (d) Shuster, D. I.; Goldstein, M. D.; Bane, P. *J. Am. Chem. Soc.* **1977**, *99*, 187. (e) Hoshino, M.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3075. (f) Goldfrey, T. S.; Porter, G.; Suppan, P, *Discuss. Faraday Soc.* **1965**, *39*, 194.

12, these two criteria cannot be invoked. Instead, we first propose that spatial location of the two aryl π-systems including the two chromophores is very critical for intramolecular interaction between phthaloyl and aryl amino groups.

Experimental Section

Apparatus. ^{1}H NMR spectra were recorded on a JEOL PS-100 spectrometer and chemical shifts were reported in parts per million on the δ scale from internal tetramethylsilane. Mass spectra were recorded on a Hitachi M-52 mass spectrometer. Infrared spectra were taken on a JASCO-402G spectrometer. UV spectra were taken on a Shimazu UV-200. Elemental analyses were performed at the micro-analytical laboratory of Kyoto University. Melting points were measured on a Yanagimoto micro melting point apparatus and uncorrected.

Preparation of Iminoquinones. A typical procedure was as follows. A mixture containing 2-phenyl-1,4-naphthoquinone (1 mmol), 4-methoxyphenyl azide (3 mmol), and Na_2CO_3 (200 mg) was heated at 80 °C for about 4 days. Products were separated by passing them through a silica gel column with 10% ether–hexane as eluents. The first fraction contained recovered azide. The second fraction contained the iminoquinone **2a**. The third fraction contained trace amounts of aminoquinone **7a**. The fourth fraction contained 2-((4-methoxyphenyl)imino)methyl-2-phenylindan-1,3-dione. Details were reported previously.[2]

General Procedure for Irradiation of 2 with Olefins. A solution in a Pyrex tube containing ca. 0.5 mmol of **2** and 25 mmol of an olefin in 25 mL of benzene under nitrogen atmosphere was irradiated with a 300-w high-pressure mercury lamp through a 5-cm thick water layer for about 80 h. Removal of the solvent and the recovered olefin at reduced pressure left a red oil which was chromatographed on a silica gel column with 10% ether–hexane or methylene chloride as the eluent. The major band contained the cycloadduct **6**, which was recrystallized from methyl alcohol.

Physical Properties of the Cycloadducts 6. 10,11-Benzo-13-(4-methoxyphenyl)-1-phenyl-13-azatetracyclo-[6.4.1.1^{3,6}.0^{2,7}]tetradecene-9,12-dione (6a). ^{1}H NMR ($CDCl_3$) δ 1.0–1.6 (m, 8), 2.70 (d, 8 Hz, 1, proton at C2), 2.98 (dd, 10 Hz, 8 Hz, 1, proton at C7), 3.43 (s, 3, OCH_3), 5.40 (d, 10 Hz, 1, proton at C8), 6.11 (d, 10 Hz, 2, a half of $NC_6H_4OCH_3$), 6.26 (d, 10 Hz, 2, a half of $NC_6H_4OCH_3$), 7.1–7.9 (m, 9, aromatic); IR (KBr) 1685 m, 1585 w, 1510 s cm^{-1}; MS (15eV), *m/e* (relative abundance) 449 (M+, 100), 327 (80), 239 (80), 210 (100). Anal. ($C_{30}H_{27}O_3N$) C, H, N.

10,11-Benzo-1-(4-chlorophenyl)-13-(4-methoxyphenyl)-13-azatetracyclo[6.4.1.1^{3,6}.0^{2,7}]tetradecene-8,11-dione (6b). ^{1}H NMR ($CDCl_3$) δ 0.8–1.8 (m, 8), 2.64 (d, 8 Hz, 1, proton at C2), 2.96 (dd, 10 Hz, 8 Hz, 1, proton at C7), 3.48 (s, 3), 5.38 (d, 10 Hz, 1, proton at C8), 6.08 (d, 9 Hz, 2, half of $NC_6H_4OCH_3$), 6.28 (d, 9 Hz, 2, a half of $NC_6H_4OCH_3$), 7.1–8.0 (m, 8); IR (KBr) 1670 s, 1585 m, 1510 s cm^{-1}; MS (15eV), *m/e* (relative intensity) 486 (19), 485 (48), 484 (44), 483 (M+, 100). Anal. ($C_{30}H_{26}O_3NCl$) C, H, N, Cl. Mp 222–224 °C.

3,4-Benzo-8-cyano-9-(4-methoxyphenyl)-1-phenyl-9-azabicyclo[4.2.1]nonene-2,5-dione (6c). ^{1}H NMR ($CDCl_3$) δ 2.40 (m, 1, proton at C7), 3.00 (m, 1, proton at C7), 3.56 (s, 3), 3.96 (dd, 8 Hz, 4 Hz, 1, proton at C8), 5.46 (dd, 10 Hz, 4 Hz, proton at C6), 6.16 (d, 9 Hz, 2, a half of $NC_6H_4OCH_3$), 6.46 (d, 9 Hz, 2, a half of $NC_6H_4OCH_3$), 7.3–8.0 (m, 9); IR (KBr) 2220 w, 1680 vs, 1585 m, 1510 vs. cm^{-1}; MS (15eV), *m/e* 408 (100). Anal. ($C_{26}H_{20}O_3N_2$) C, H, N. Mp 88–90 °C.

3,4-Benzo-8-(methoxycarbonyl)-9-(4-methoxyphenyl)-1-phenyl-9-azabicyclo[4.2.1]nonene-2,5-dione (6d). ^{1}H NMR ($CDCl_3$) δ 2.22 (ddd, 14 Hz, 8 Hz, 2 Hz, 1, proton at C7), 3.00 (m, 1, proton at C7), 3.20 (s, 3, CO_2CH_3), 3.44 (s, 3, OCH_3), 3.80 (dd, 8 Hz, proton at C8), 5.26 (dd, 2 Hz, 8 Hz, 1, proton at C6), 6.1–6.4 (m, 4), 7.2–8.0 (m, 9); IR (CCl_4) 1740 s, 1680 s, 1590 m, 1510 s cm^{-1}; MS (15eV), *m/e* (relative intensity) 442 (10), 441 (M+, 25), 116 (100). Anal. ($C_{27}H_{23}O_5N$) C, H, N. Mp 183–185 °C.

3,4-Benzo-9-(4-methoxyphenyl)-1-phenyl-8-(1-propenyl)-9-azabicyclo[4.2.1]nonene-2,5-dione (6e). ^{1}H NMR ($CDCl_3$) δ 1.60 (d, 7 Hz, 3, CH_3), 1.9–2.9 (m, 3), 3.44 (s, 3, OCH_3), 5.1–5.6 (m, 3, vinyl proton plus proton at C6), 6.1–6.4 (m, 4), 7.1–7.9 (m, 9); IR (NaCl) 1680 vs, 1590 s, 1510 s cm^{-1}; MS (15eV), *m/e* (relative intensity) 424 (9), 423 (M+, 21), 250 (100). Anal. ($C_{28}H_{25}O_3N$) C, H, N.

3,4-Benzo-1,8α-diphenyl-8β-methyl-9-(4-methoxyphenyl)-9-azabicyclo[4.2.1]nonene-2,5-dione (6f). ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 3, CH_3), 2.12 (d, ABq, 10 Hz, 16 Hz, 1, proton at C7α), 3.20 (d, ABq, 6 Hz, 16 Hz, 1, proton at C7β), 3.44 (s, 3, OCH_3), 5.63 (dd, 6 Hz, 10 Hz, 1, proton at C6), 6.10 (d, 9 Hz, 2), 6.24 (d, 9 Hz, 2), 7.0–8.0 (m, 9); IR (KBr) 1685 m, 1590 w, 1510 m, cm^{-1}; MS (20eV), *m/e* (relative intensity) 473 (M+, 8), 210 (100). Anal. ($C_{32}H_{27}O_3N$) C, H, N. Mp 178–179 °C.

3,4-Benzo-1,8β-diphenyl-8α-methyl-9-(4-methoxyphenyl)-9-azabicyclo[4.2.1]nonene-2,5-dione (6g). ^{1}H NMR ($CDCl_3$) δ 1.36 (s, 3, Me), 2.48 (d, ABq, 9 Hz, 16 Hz, 1, proton at C7), 2.76 (d, ABq, 9 Hz, 16 Hz, 1, proton at C7), 3.48 (s, 3, OCH_3), 5.44 (dd, 9 Hz, 9 Hz, 1, proton at C6), 6.02 (d, 9 Hz, 2), 6.24 (d, 9 Hz), 7.0–8.0 (m, 9); IR (KBr) 1685 m, 1590 w, 1510 m cm^{-1}; MS (15eV), *m/e* (relative intensity) 473 (M+, 8), 210 (100); mp 84–85 °C.

3,4-Benzo-7β,8α-bis(methoxycarbonyl)-9-(4-methoxyphenyl)-1-phenyl-9-azabicyclo[4.2.1]nonene-2,5-dione (6h). ^{1}H NMR ($CDCl_3$) δ 3.54 (s, 3, CO_2CH_3), 3.54 (s, 3, $PhOCH_3$), 3.6 (m, 1, proton at C7α), 4.04 (d, 8 Hz, 1, proton at C8β), 5.56 (d, 4 Hz, 1 proton at C6), 3.80 (s, 3, CO_2CH_3), 6.10 (d, 9 Hz, 2), 6.24 (d, 9 Hz, 2), 7.0–8.0 (m, 9); IR (KBr) 2940 w, 1730 vs, 1680 s, 1582 w cm^{-1}; MS (15eV), *m/e* (relative intensity) 500 (29), 499 (M+, 100), 467 (26), 222 (91). Anal. ($C_{29}H_{25}O_7N$) C, H, N. Mp 64–66 °C.

3,4-Benzo-7α,8β-bis(methoxycarbonyl)-9-(4-methoxyphenyl)-1-phenyl-9-azabicyclo[4.2.1]nonene-2,5-dione (6i). ^{1}H NMR ($CDCl_3$) δ; 3.32 (s, 3, CO_2CH_3), 3.54 (s, 3, $PhOCH_3$), 3.76 (s, 3, CO_2CH_3), 4.24 (m, 2, protons at C7β and C8α), 5.38 (d, d, 5 Hz, 2 Hz, 1, proton at C6), 6.10 (d, 9Hz, 2), 6.24 (d, 9 Hz, 2), 7.0–8.0 (m, 9). IR (KBr) cm^{-1}; 2940 w, 1730 vs, 1680 s, 1580 w, 1505 s. MS (15eV) *m/e* (rel. intensity); 500 (29), 499 (M+, 100), 467 (26), 222 (90). Mp. 127.5–129 °C.

3,4-Benzo-7β,8β-bis(methoxycarbonyl)-9-(4-methoxyphenyl)-1-phenyl-9-azabicyclo[4.2.1]nonene-2,5-dione (6i). ^{1}H NMR ($CDCl_3$) δ 3.24 (s, 3, CO_2CH_3), 3.4 (m, 1, proton at C7α), 3.56 (s, 3, $PhOCH_3$), 3.80 (s, 3, CO_2CH_3), 4.12 (d, 8 Hz, 1, proton at C8α), 6.02 (d, 8 Hz, 1, proton at C6), 6.10 (d, 9 Hz, 2), 6.24 (d, 9 Hz, 2), 7.0–8.0 (m, 9); IR (KBr 2870 m, 1745 vs. 1720 w, 1685 s, 1580 m; MS (15eV), *m/e* (relative intensity) 500 (30), 499 (M+, 100); mp 200–203 °C.

Irradiation of 1b with Dimethyl Fumarate and Dimethyl Maleate. A benzene solution of **1b** (300 mg) and dimethyl fumarate (500 mg) was irradiated through a 1-cm $CuSO_4$ filter for 22 h. Solvent and the olefin was distilled off at a reduced pressure. The residual brown oil was distilled by using a Kugelrohr distillation apparatus. Starting **1b** was recovered at 140–170 °C (0.001 torr). By washing the residue with diethyl ether colorless crystals of **5c** were obtained and they were recrystallized from methyl alcohol. Conversion was 68% and the yield of **5c** was 32.4%. Spectral data of **5c** was as follows: ^{1}H NMR ($CDCl_3$) δ 3.24 (s, 3, CO_2CH_3), 3.60 (s, 3, CO_2CH_3), 4.2 (m, 2), 5.44 (m, 1), 7.2–7.4, 7.5–8.0 (m, 9); IR (KBr) 1750 vs, 1732 s, 1690 s, 1490 w, 1445 s, 1435 s cm^{-1}; MS (15eV), *m/e* (relative intensity) 394 (M+, 100). Anal. ($C_{22}H_{18}O_7$) C, H. Mp 176–178 °C.

A benzene solution of **1b** (500 mg) and dimethyl maleate (500 mg) was irradiated through a 1-cm $CuSO_4$ filter for 12 h. Solvent, olefin, and recovered **1b** were distilled off at a reduced pressure (0.001–0.005 torr). The residue was recrystallized from methyl alcohol and **5d** was obtained as colorless crystals in a yield of 100%. Spectral data of **5d** was as follows: ^{1}H NMR ($CDCl_3$) δ 3.26 (s, 3, CO_2CH_3), 3.75 (s, 3, CO_2CH_3), 3.5 (dd, 7.5 Hz, 7.7 Hz, 1), 4.34 (d, 7.7 Hz, 1), 5.66 (d, 7.5 Hz, 1), 7.2–7.4, 7.5–8.0 (m, 9); IR (KBr) 1790 vs, 1730, 1685 s, 1270 vs cm^{-1}; MS (15eV), *m/e* (relative intensity) 394 (M+, 100). Anal. ($C_{22}H_{18}O_7$) C, H. Mp 178–180 °C.

Irradiation of 1a with Dimethyl Fumarate and Dimethyl Maleate. A benzene solution of **1a** (200 mg) and dimethyl fumarate (500 mg) was irradiated through a 1-cm $CuSO_4$ filter for 26 h. Solvent and olefin were distilled off at a reduced pressure. Recovered **1a** was distilled off by using the Kugelrohr distillation apparatus at 120–130 °C (0.001 torr). The residue was recrystallized from methyl alcohol and **5a** was obtained in a yield of

Table X[a]

no.	δ (ppm)	J, Hz	S value	assignment
A	0.79 (d)	~12	1.94	
B	0.95 (d)	~12	0.75	H^5 exo or endo
C	1.03 (dd)	~10, ~2	0.60	or H^6 exo or
D	1.19 (dd)	~10, ~2	0.00	endo
E	1.55 (m)	~2, ~2, ~2.9, ~2.9	0.30	H^7 anti and syn
F	2.50 (d)	~2.9	1.13	H^4
G	2.65 (d)	~2.9	1.93	H^1 (=H^d)
H	2.72 (d)	9.77	0.83	H^3 (=H^c)
I	2.99 (dd)	9.77, 10.38	1.01	H^2 (=H^b)
J	3.50 (s)		0.14	OCH_3
K	5.42 (d)	10.38	3.30	H^a
L	6.14 (d)	9.16	0.50	$NC_6H_4OCH_3$
M	6.29 (d)	9.16	0.74	

[a] The best fit of experimental S values with those of calculated values (Yamazaki A. *Kagaku (Kyoto)* **1974**, *29*, 349; Roberts J. D., Hawkes G. E., Roberts A. W., Roberts D. W., *Tetrahedron* **1974**, *30*, 1833.) was found when the exo-anti configuration was assumed (correlation coefficient = 0.87). The correlation coefficients for other configurations were smaller (for exo-syn 0.78 and for endo-anti 0.77).

70%. The physical data were identical with that reported previously.[1b]

A benzene solution of **1a** (400 mg) and dimethyl maleate (1 g) was irradiated through a 1-cm $CuSO_4$ filter for 10 h. Solvent and olefin were distilled off at a reduced pressure. Recovered **1a**, **5a**, and **5b** were separated by Kugelrohr distillation at 0.001 torr. Compound **5a** was distilled at 140 °C and **5b** was distilled at 150–170 °C.

Estimation of Electron Affinities of 1b and 2a. Electron affinities of **1b** and **2a** were estimated by using the following equation.[17] $h\nu_j - h\nu_i = EA_i - EA_j$; $h\nu$ is the energy of the longest wavelength transition of the CT absorption, EA is electron affinity, and subscript i denotes the sample and j the reference. The concentration of hydroquinone dimethyl ether was 0.5 M and of **2a** and **1b** 1 mM. The solution of **2a** or **1b** without the donor was placed in the reference. Reference acceptor was 1 mM of 1,4-naphthoquinone. The CT band appeared at 445 nm, 418 nm, 418 nm respectively for 1,4-naphthoquinone, **2a**, and **1b**. By the use of the electron affinity of 1,4-naphthoquinone (1.26 eV),[9a] the electron affinities of **2a** and **1b** were obtained as 1.08 eV.

Reactivity. Quantum yields were measured by using a ferrioxalate actinometer in a benzene solution of a known amount of olefin concentration and 1 mM of **1** or **2**. Quantum yields were dependent upon the amount of olefins in the reacting solutions and were measured at the olefin concentration of 20, 50, 80, 160, and 320 mM. Irradiation was undertaken in a merry-go-round by using 313 nm light for 1 h in the case of **1b** or for 40–80 h in the cases of **2a**. The amounts of cycloadducts were determined by HPLC with a column of μ-Porasil analytical and 5%–20% ether–hexane as eluents. Conversion did not exceed 10%.

Registry No. **1a**, 53948-58-6; **1b**, 13369-47-6; **2a**, 79060-54-1; **2b**, 79060-50-7; **5a**, 63689-05-4; **5b**, 87420-83-5; **5c** (isomer 1), 87373-38-4; **5c** (isomer 2), 87420-85-7; **5d**, 87420-84-6; **6a**, 87373-39-5; **6b**, 87373-40-8; **6c**, 87373-41-9; **6d**, 87373-42-0; **6e**, 87373-43-1; **6f**, 87373-44-2; **6g**, 87420-86-8; **6h**, 87373-45-3; **6i**, 87420-87-9; **6j**, 87420-88-0; **6k**, 87373-46-4; norbornene, 498-66-8; α-methylstyrene, 98-83-9; methyl acrylate, 96-33-3; dimethyl acrylate, 624-48-6; dimethyl fumarate, 624-49-7; 1,3-pentadiene, 504-60-9; acrylonitrile, 107-13-1.

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(19) Shift reagent experiments were performed on a JEOL JNM-FX400 400-MHz ^1H NMR apparatus with $Eu(fod)_3$ as a shift reagent. The results are given in Table X.

Dienophilic Properties of Phenyl Vinyl Sulfone and *trans*-1-(Phenylsulfonyl)-2-(trimethylsilyl)ethylene. Their Utilization as Synthons for Ethylene, 1-Alkenes, Acetylene, and Monosubstituted Alkynes in the Construction of Functionalized Six-Membered Rings via [4 + 2] π Cycloaddition Methodology

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Useful procedures for effecting the indirect capture of ethylene, acetylene, 1-alkenes, and monosubstituted alkynes in Diels–Alder cycloadditions have been developed. In the first sequence, phenyl vinyl sulfone is shown to enter into [4 + 2] π reactions as a moderately reactive dienophile and to do so with very good regioselectivity. The resulting adducts can be directly desulfonated or alkylated prior to such reduction. A wide range of functional groups can be appended in this fashion at a specific locus within the newly formed six-membered ring. When the analogous chemistry is applied to *trans*-1-(phenylsulfonyl)-2-(trimethylsilyl)ethylene (**2**), adducts result which undergo ready fluoride ion induced elimination with efficient introduction of a double bond. The use of **2** and its d_2 derivative is highlighted by the synthesis of several functionalized dibenzobarrelenes.

The low reactivity of unadorned alkenes and alkynes as dienophilic reagents ranks as one of the foremost limitations of Diels–Alder cycloaddition chemistry. To achieve the [4 + 2] π condensation of ethylene to butadienes, temperatures of 175 °C and pressures of 6000 psi or more are required.[1,2] Somewhat less forcing conditions are necessary for allyl compounds,[3,4] although yields are often little improved. More constrained olefins have been reported to react with highly activated dienes with greater facility,[5,6] although such behavior is hardly typical. The

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