= 15.6, 7.0 Hz, H_3), 6.24 (dd, J = 10.5, 15.3 Hz, H_9), 6.00 (m, H_{10}), 5.75 (m, 2 H, H_2, H_{11}), 5.37 (d, J = 15.3 Hz, H_8), 3.86 (m, 4 H, OCH_2CH_2O), 3.68 (s, 3 H, OCH_3), 2.18 (m, 2 H, allylic CH_2), 1.72 (dd, J = 6.8, 1.3 Hz, CH_3), 1.66 (m, 2 H), 1.54 (m, 2 H); IR (CCl_4) 3022, 1723, 1660 cm^{-1}; mass spectrum, m/e 266 (parent ion); high-resolution mass spectrum calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1519.

Methyl (*Z,E,E*)-7-Oxododeca-2,8,10-trienoate Ethylene Glycol Ketal (24). Triene **18a** (49.1 mg, 0.22 mmol) was oxidized with Ag_2CO_3 on Celite (0.923 g, 1.62 mmol, 10 mL of benzene)[22] as described for **46**, giving 50 mg of crude product. This material was partially purified by bulb-to-bulb distillation (150 °C (0.1 mm)), giving 45.7 mg of methyl (*Z,E,E*)-7-oxododeca-2,8,10-trienoate (94%). The distilled product still contained a small amount of impurities which were removed by preparative TLC on a 10 × 20 cm 0.25-mm silica gel plate eluted with 1:1 ether–hexane. This gave 31.0 mg (64%) of pure ketone: mp 34–37 °C; NMR ($CDCl_3$, 250 MHz) δ 7.09 (m, H_9), 6.21 (m 3 H, H_3, H_{10}, H_{11}), 6.02 (d, J = 15.1 Hz, 1 H, H_8), 5.76 (dt, J = 11.6, 1.6 Hz, H_2), 3.66 (s, 3 H, OCH_3), 2.64 (dq, J = 1.6, 7.5 Hz, 2 H, allylic CH_2), 2.56 (t, J = 7.2 Hz, 2 H, $COCH_2$), 1.83 (d, J = 5.1 Hz, CH_3), 1.74 (m, 2 H); IR (CCl_4) 3024, 1720, 1685, 1667, 1636, 1593 cm^{-1}; mass spectrum, m/e 222 (parent ion); high-resolution mass spectrum calcd for $C_{13}H_{18}O_3$ 222.1256, found 222.1236.

Ketal **24** was prepared by using the procedure described for **22**. To a solution of 17.8 mg of the ketone described in the previous paragraph (0.08 mmol) in 0.5 mL of dry THF at 23 °C was added 0.4 mL of 2-methoxy-1,3-dioxolane (0.42 mmol), 0.3 mL of ethylene glycol (0.54 mmol), and one small crystal of p-$TsOH{\cdot}H_2O$.[34] The reaction was monitored by analytical TLC (1:2 ether–hexane: R_f(ketone) 0.31; R_f(**24**) 0.47). When complete (18 h in this case), the reaction was worked up in the usual manner. The crude product was purified by PTLC (one 0.5-mm silica gel plate, 1:2 ether–hexane), giving 14.1 mg of ketal **24** (68%): NMR ($CDCl_3$, 250 MHz) δ 6.0–6.4 (m, 3 H, H_3, H_9, H_{10}), 5.74 (m, 2 H, H_{11}, H_2), 5.39 (d, J = 15.1 Hz, H_8), 3.87 (m, 4 H, OCH_2CH_2O), 3.67 (s, 3 H, OCH_3), 2.64 (dq, J = 1.6, 7.5 Hz, 2 H, allylic CH_2), 1.74 (dd, J = 6.7, 1.3 Hz, 3 H, CH_3), 1.50 (m, 2 H); IR (CCl_4) 3023, 1729, 1644 cm^{-1}; mass spectrum, m/e 266 (parent ion); high-resolution mass spectrum calcd for $C_{15}H_{22}O_4$ 266.1518, found 266.1529.

Acknowledgment. Acknowledgment is made to the NIH (Grant No. GM26782), to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corp. for support of this research. We are grateful to Dr. Catherine Costello for measurement of high-resolution mass spectra.

Reagent Design and Study of *p*-Benzoquinone Derivatives as Highly Reactive Electron-Attracting Dienophiles.[1] A Promising Class of Reagents (Synthons) for Cycloaddition

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Contribution from the Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical Sciences, Kyushu University, Fukuoka 812, Japan, and Department of Chemistry, Faculty of Sciences, Hokkaido University, Sapporo 060, Japan. *Received January 12, 1981*

Abstract: *p*-Benzoquinone-2,3-dicarboxylic anhydride (**4**) and *N*-phenylimide (**5**) were prepared by oxidation of the corresponding hydroquinones. Compounds **4** and **5** are found to have high reactivities toward electron-rich dienes and trienes such as norbornadiene, 6,6-dimethylfulvene, and cycloheptatriene; the selectivities are discussed in terms of frontier molecular orbital theory, indicating that both compounds are powerful electron-attracting dienophiles for the cycloadditions. The stereochemistry of the adducts was determined by spectral inspections and chemical transformation leading to the cage compounds.

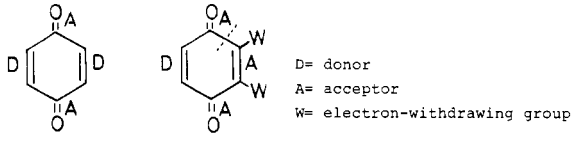
Interest in strained cage molecules[3] has accelerated greatly during the past decade, since these compounds continue to play an important role in the understanding of many aspects of organic chemistry. Thus, synthetic efforts in this area have been extensive. One of the general methods used to prepare such systems involves a photochemical intramolecular [2 + 2] cycloaddition of *p*-benzoquinone (**1**) to cyclic dienes.[4] *However, p-benzoquinone behaves only as a weak dienophile in the Diels–Alder reaction and is rather inert to homodienes, conjugated medium-ring polyenes such as norbornadiene, cycloheptatriene, and tropone even under drastic conditions. Therefore, it appears worthwhile to attempt to use this versatile p-benzoquinone derivative as a dienophile component in the Diels–Alder reactions.*

Results and Discussion

Theoretical Expectations. On the basis of the concept of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) relationship of the frontier-controlled pericyclic reactions,[5] we considered that introduction of strong electron-attracting substituents in *p*-benzoquinone would cause a lowering of the LUMO energy. This would result in enhancement of the reactivity of *p*-benzoquinone which would accelerate the pericyclic reaction to the polyenes. These ideas are also applicable to variations of the olefinic reactants in the pericyclic reactions. Since the $_{\pi}4_s + _{\pi}2_s$ transition state of the cycloaddition of an electron-rich butadiene and an electron-poor ethylene is isoconjugate to a substituted benzene, the reaction proceeds via aromatic transition states and the aromaticity is not destroyed by substituents.[6,7]

Recently, Inagaki et al.[8] proposed the degree of cyclic electron delocalization to be a function of the mode of the donor–acceptor

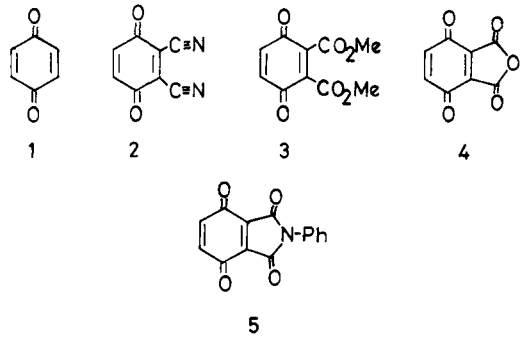
Chart I



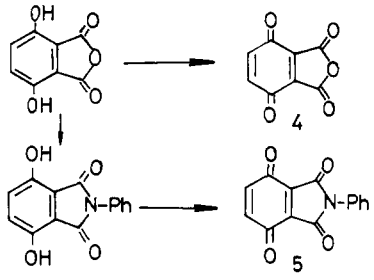
(1) Some of the work described in this paper has appeared in preliminary form: (a) Morita, S.; Fukushima, S.; Kanematsu, K. *Tetrahedron Lett.* **1979**, 2151. (b) *Heterocycles* **1979**, *12*, 481.
(2) (a) Kyushu University; (b) Hokkaido University.
(3) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978.
(4) Warrener, R. N.; McCay, I. W.; Paddon-Row, M. N. *Aust. J. Chem.* **1977**, *30*, 2189, and references cited therein.
(5) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4693.
(6) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761.
(7) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1191.
(8) Inagaki, S.; Hirabayashi, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7418.

0002-7863/81/1503-5211$01.25/0

Chart II



Scheme I



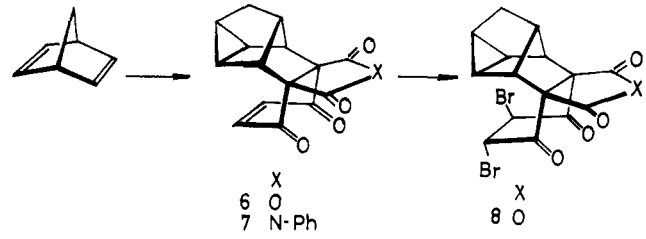
arrangements of component systems as well as orbital phase continuity requirements: *p*-benzoquinone (**1**) corresponds to a discontinuous conjugation mode and cyclic conjugation is not significant (Chart I).

Whereas the electron-attracting substituent effect on *p*-benzoquinone (**1**) originates by emphasizing the electron-localizing modes, the cyclic conjugation is continuous, but the orbital phase continuity requirements are not satisfied as shown in Chart I.

To the best of our knowledge, there are few reports concerning Diels–Alder reactions of the quinones containing electron-attracting substituents such as chloranil and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) with cyclic dienes.[9] However, these quinones are often the reagents of choice for dehydration and selective oxidation in organic synthesis. In fact, the reaction of chloranil or DDQ with cycloheptatriene led to tropylium salt[10] instead of a cycloadduct.

From these considerations, *p*-benzoquinone-2,3-dicarboxylic anhydride (PBA, **4**) and *p*-benzoquinone-2,3-dicarboxylic *N*-phenylimide (PBI, **5**) seemed to be good models for this study (Chart II). This prediction is beautifully demonstrated by MNDO calculations[11] which are summarized in Table I. In this connection, Cooper and Dewar et al.[11] have reported a value for the electron affinity of *p*-benzoquinone (**1**) which is in very close agreement with the calculated MNDO adiabatic value of −1.88 eV. Figure 1 shows the frontier molecular orbitals (FMO) of the *p*-benzoquinone derivatives **1**–**5** wherein the signs of the p_z coefficients are represented by the diameters of the circles at each atom: the LUMOs of PBA (**4**) and PBI (**5**) have the largest coefficients at C-2 and C-3, respectively, and hence the cycloaddition reactions will occur regioselectivity at the same positions toward polyenes.[12] Furthermore, the magnitudes of LUMO coefficients at C-1 and C-4 are larger than at C-9 and C-11, and thus endo addition with respect to the benzoquinone moiety should

Scheme II



Scheme III

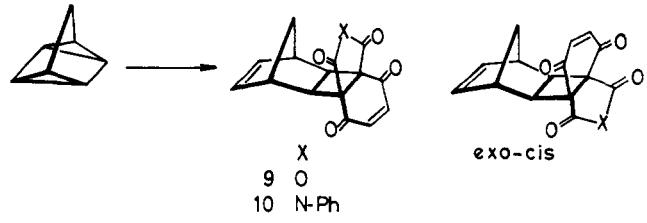


Chart III

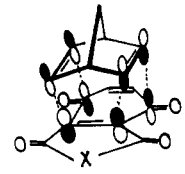
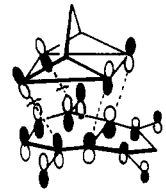


Chart IV



be predicted by means of secondary orbital interactions.

Preparation of PBA and PBI. Oxidation of hydroquinone-2,3-dicarboxylic anhydride with fuming nitric acid according to Tiele et al.[13] gave only a trace of PBA (**4**). However, PBA (**4**) was obtained in a moderate yield by using 2 M phenyliodide ditrifluoroacetate $[C_6H_5I(OCOCF_3)_2]$[14] in benzene at room temperature. On the other hand, heating hydroquinone-2,3-dicarboxylic anhydride with aniline in acetic acid afforded hydroquinone-2,3-dicarboxylic *N*-phenylimide, whose treatment with nitrogen dioxide or phenyliodine ditrifluoroacetate in carbon tetrachloride gave PBI (**5**) in quantitative yield (Scheme I).

Cycloadditivity of PBA and PBI and Structure Elucidation of the Adducts. With Norbornadiene and Quadricyclane. When norbornadiene was added to PBA (**4**)[15] and PBI (**5**) suspended in solvents such as nonpolar benzene, chloroform, or acetonitrile at refluxing temperature, only the 1:1 homo-Diels–Alder adducts **6** and **7** were formed, respectively. It is interesting that the exclusive formation of these adducts could be explained as the result of concerted fashion, since similar reaction of norbornadiene with substituted acetylenic dienophile gave the homo-Diels–Alder adduct together with [2 + 2]π cycloadduct and Wagner–Meerwein-type rearrangement product via an ionic intermediate.[16] The endo stereochemistry of the adducts was confirmed by ^{1}H NMR spectral comparison with that of **8**, prepared by bromination of

(9) (a) Gaertner, R. *J. Am. Chem. Soc.* **1954**, *76*, 6150. (b) Pointer, D. J.; Wilford, J. B.; Hodder, O. J. R. *J. Chem. Soc. B* **1971**, 2009. (c) Kuroda, S.; Funamizu, M.; Kitahara, Y. *Tetrahedron Lett.* **1975**, 1973, and references cited therein.

(10) Reid, D. H.; Fraser, B. B.; Molloy, B. B.; Payne, H. A. S.; Sutherland, R. G. *Tetrahedron Lett.* **1961**, 530.

(11) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) *Ibid.* **1977**, *99*, 4907. (c) Dewar, M. J. S.; Rzepa, H. S. *Ibid.* **1978**, *100*, 784. (c) Cooper, C. D.; Naff, W. T.; Compton, R. N. *J. Chem. Phys.* **1975**, *63*, 2752.

(12) Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: 1976.

(13) Tiele, J.; Gunther, F. *Justus Liebigs Ann. Chem.* **1906**, *349*, 66.

(14) Spyroudis, S.; Varvoglis, A. *Synthesis* **1975**, *445*.

(15) Kinetic measurements for Diels–Alder reaction of PBA with some dienes have been described, but no systematic investigation was undertaken. See: (a) Sauer, J.; Schröder, B. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 711. (b) Sauer, J. *Ibid.* **1967**, *6*, 16.

(16) Sasaki, T.; Eguchi, S.; Sugimoto, M.; Hibi, F. *J. Org. Chem.* **1972**, *37*, 2317.

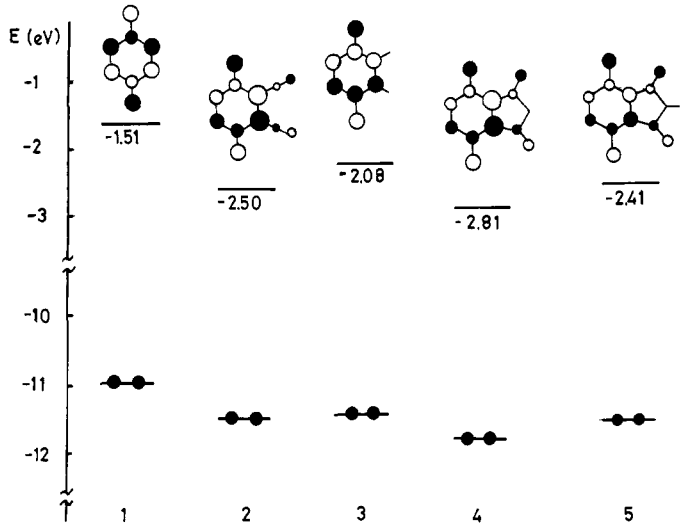
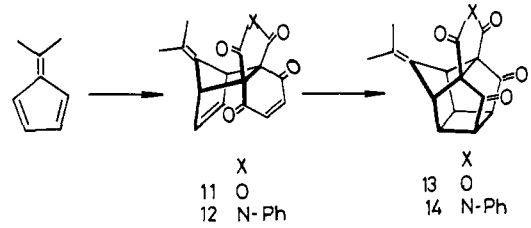
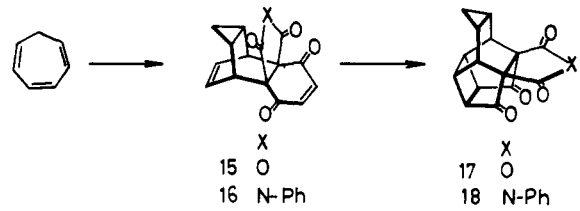


Figure 1. FMO energy levels and coefficients by MNDO MO method.

Scheme IV



Scheme V

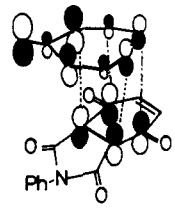


6 (Scheme II); the cyclopropyl signals at δ 1.40 (m, 2 H) and 1.64 (m, 1 H) in **8** are shifted downfield relative to those of the adducts, whereas the other signals in **8** appear at approximately the same positions as those of **6**. Thus, the preferential formations of the endo $[2 + 2 + 2]\pi$ cycloadducts **6** and **7** might be controlled by the secondary interactions of the frontier orbitals between the reactants in the transition state as depicted in Chart III.

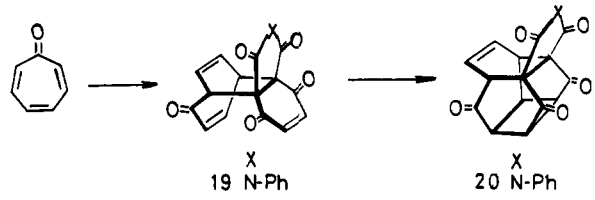
Similar treatments of quadricyclane with PBA (**4**) and PBI (**5**) gave the adducts **9** and **10** in quantitative yields, respectively (Scheme III). The adducts **9** and **10** were determined to have the exo-trans configuration by comparison of their ^{1}H NMR spectra with those of the exo-trans adducts of quadricyclane and *p*-benzoquinone, indicating a skeletal similarity.[17] Therefore, the alternative exo-cis structure could be ruled out. The exclusive formation of the exo-trans adducts can be also rationalized in terms of the secondary orbital interactions (antibonding) between reactants in the endo transition state as depicted in Chart IV.

With 6,6-Dimethylfulvene, Cycloheptatriene, and Tropone. In a similar manner, the reactions of 6,6-dimethylfulvene and cycloheptatriene gave the corresponding 1:1 adducts **11**, **12**, **15**, and **16** in quantitative yields with immediate disappearance of PBA (**4**) and PBI (**5**) (Schemes IV and V). The edno configurations of the adducts were fully confirmed by chemical transformation. Irradiations of the adducts **11**, **12**, **15**, and **16** in acetone solution

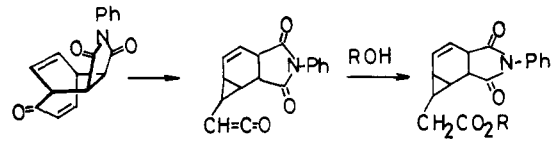
Chart V



Scheme VI



Scheme VII



(Pyrex filter, 100-W high-pressure mercury lamp) afforded the cage compounds **13**, **14**, **17**, and **18** in quantitative yields. Structure assignments for the photocage products were determined on the basis of the ^{1}H NMR and IR spectral inspections. These cage compounds showed characteristic bands in the IR at 1760–1770 cm^{-1} (five-membered carbonyl groups) rather than the enedione carbonyl groups at 1670–1680 cm^{-1}. No olefinic protons were visible in the ^{1}H NMR. These spectral data are summarized in Table II.

These results are in sharp contrast to Takeshita's conclusion for the reaction of cycloheptatriene and *p*-benzoquinone. The thermal cycloaddition reaction of cycloheptatriene and *p*-benzoquinone afforded vicinal ditropylation product together with a trace of the 1:1 adduct (only 1%!) even under more drastic conditions.[18]

On the other hand, tropone was inert to PBI (**5**) in benzene at room temperature, but it reacted only in chlorobenzene at elevated temperature (about 110 °C). However, with PBA (**4**), only intractable materials were obtained. Adduct **19** was concluded to be the unexpected $[4 + 2]\pi$ cycloadduct by ^{1}H NMR. The ^{1}H NMR spectrum of the adduct exhibited a characteristic pattern of the known $[4 + 2]\pi$ tropone adducts.[19] The stereochemistry of the adduct could be assigned the exo form of the enedione moiety, because the IR spectrum of the photoinduced cage compound **20** exhibited the six- and five-membered nonconjugated carbonyl absorptions at 1730 and 1765 cm^{-1} instead of the conjugated carbonyl absorptions at 1660 and 1680 cm^{-1} in **19**.

This fact could be explained by assuming the initial formation of the endo adduct assisted by a secondary orbital effect, as depicted in Chart V, followed by redissociation at higher reaction temperature into the thermodynamically more stable adduct **19** (Scheme VI). It is interesting that the photolysis of **19** give only the cage ketone **20** even in protic solvent such as methanol, while similar irradiation of the adduct of tropone and *N*-phenylmaleimide gave only the [3.3] photorearrangement product (Scheme VII).[20] The reaction conditions and the yields of the adducts for these cycloaddition reactions as described above are summarized in Table III.

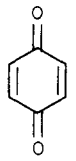
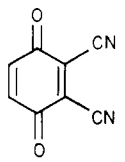
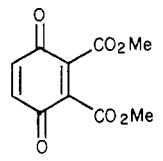
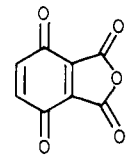
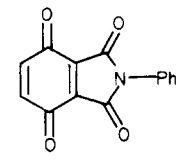
(17) Kaupp, G.; Prinzbach, H. *Chem. Ber.* **1971**, *104*, 182. More vigorous conditions were required for the reaction of quadricyclane with *p*-benzoquinone. The adduct was assigned the exo-trans configuration by ^{1}H NMR inspection.

(18) Takeshita, H.; Mori, A.; Mametsuka, H. *Chem. Lett.* **1976**, 445.

(19) (a) Ito, S.; Takeshita, H.; Shoji, T. *Tetrahedron Lett.* **1969**, 1815. (b) Sasaki, T.; Kanematsu, K.; Hayakawa, K. *J. Chem. Soc. C* **1971**, *2142*.

(20) Sasaki, T.; Kanematsu, K.; Hayakawa, K. *J. Chem. Soc., Perkin Trans. 1* **1972**, 786.

Table I. Calculated LUMO Energies and Coefficients of *p*-Benzoquinone and Its Derivatives by MNDO Methods

		 (1)		 (2)		 (3)[a]		 (4)		 (5)
energy		−1.50714 eV		−2.50252 eV		−2.07844 eV		−2.81086 eV		−2.41310 eV
atomic orbital	C_1	0.33672	C_1	−0.26752	C_1	−0.30532	C_1	−0.23257	C_1	−0.24656
	C_2	0.35756	C_2	−0.48421	C_2	−0.44474	C_2	−0.51604	C_2	−0.49880
	C_3	−0.35757	C_3	0.48421	C_3	0.44462	C_3	0.51605	C_3	0.49873
	C_4	−0.33671	C_4	0.26752	C_4	0.30534	C_4	0.23257	C_4	0.24655
	C_5	−0.35760	C_5	0.23065	C_5	0.28888	C_5	0.18280	C_5	0.20310
	C_6	0.35759	C_6	−0.23065	C_6	−0.28893	C_6	−0.18280	C_6	−0.20310
	O_7	−0.36180	O_7	0.31610	O_7	0.34446	O_7	0.29487	O_7	0.30414
	O_8	0.36179	O_8	−0.31610	O_8	−0.34446	O_8	−0.29487	O_8	−0.30412
			C_9	0.06860			C_9	0.14984	C_9	−0.14992
			N_{10}	−0.19013			C_{10}	−0.00001	O_{10}	0.18485
			C_{11}	−0.06860			C_{11}	−0.14986	C_{11}	0.14992
			N_{12}	0.19013			O_{12}	0.19182	O_{12}	−0.18480
							O_{13}	−0.19180	N_{13}	0.00004

[a] Coefficients of the ester groups are neglected.

Table II. ^{1}H NMR and IR Data for Photocage Compounds

compd	chemical shifts,[a] δ (*J* in hertz)	IR (C=O), cm^{-1} (Nujol) (cage ketones)
13	1.80 (s, 6 H, Me 2), 3.20 (m, 2 H), 3.44 (m, 2 H), 4.04 (m, 2 H)	1770
14	1.77 (s, 6 H, Me 2), 3.20 (m, 2 H), 3.33 (m, 2 H), 3.88 (m, 2 H), 7.12–7.50 (m, 5 H, phenyl)	1760
17	0.48 (m, 2 H), 0.90 (m, 2 H), 2.44 (m, 2 H), 2.58 (m, 2 H), 2.84 (m, 2 H)	1765
18	0.50 (m, 2 H), 1.05 (m, 2 H), 2.56 (m, 2 H), 2.82 (m, 2 H), 3.10 (m, 2 H), 7.20–7.50 (m, 5 H, phenyl)	1760
20	3.00–3.62 (m, 6 H), 6.12 (dd, *J* = 10.0, 8.0, 1 H, olefinic), 6.40 (m, 1 H, olefinic), 7.08–7.52 (m, 5 H, phenyl)	1730,[b] 1765

[a] Solvent CD_3COCD_3. [b] Overlapping with imide carbonyl.

From the facts stated above, we can draw the following conclusion: the source of the high reactivity and specificity of PBA and PBI in the cycloadditions will not only be due to the donor–acceptor frontier orbital interactions between reactants but also to the effectiveness of the largest magnitude of the LUMO coefficients at C-2 and C-3 of the substituted quinones assisted by the effectiveness of the secondary orbital interactions. However, tropone with a low HOMO energy level[21] shows little reactivity toward electron-deficient PBA and PBI in the cycloaddition reactions.

Experimental Section

The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The UV spectra were determined with a Hitachi EPS-3T spectrophotometer. The ^{1}H NMR spectra were taken with a JEOL PS-100 spectrometer with Me_4Si as an internal standard, and the chemical shifts are expressed in δ values. The IR spectra were taken with a JASCO IR A-1 infrared spectrophotometer. Mass spectra were obtained with a JEOL-01SG double-focusing spectrometer operating at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200 °C.

Preparation of PBA (4). A mixture of hydroquinone-2,3-dicarboxylic anhydride (5.08 g, 0.28 mol) and phenyliodine ditrifluoroacetate (23.9 g, 0.56 mol) in benzene (40 mL) was stirred for 1 h at room temperature. The precipitated red solids were filtered and purified by recrystallization from acetone to give **4** (3.4 g, 68%) as orange plates, mp 235 °C dec: IR (Nujol) 1800, 1680 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.10 (s); mass spectrum (*m*/*z*) 178 (M+). Anal. ($C_8H_2O_5$). C, H.

Preparation of Hydroquinone-2,3-dicarboxylic *N*-Phenylimide. A mixture of hydroquinone-2,3-dicarboxylic anhydride (1.8 g, 0.01 mol) and aniline (1.0 g, 0.01 mol) in acetic acid (10 mL) was heated at 100 °C for 2 h. The solution was poured into water, and the precipitates were removed by filtration and then recrystallized from acetic acid to give hydroquinone-2,3-dicarboxylic *N*-phenylimide (1.9 g, 75%) as colorless prisms, mp 255–257 °C. Anal. ($C_{14}H_9NO_4$). C, H, N.

Preparation of PBI (5). (a) To a solution of hydroquinone-2,3-dicarboxylic *N*-phenylimide (2.55 g, 0.01 mol) in CCl_4 (20 mL) was added dropwise a solution of N_2O_4 (1 mL) in CCl_4 (10 mL). Workup as described above gave PBI (**5**) (2.4 g, 94%) as orange crystals, mp 235–238 °C; IR (Nujol) 1730, 1600 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.12 (s, 2H), 7.02–7.70 (m, 5 H, phenyl); mass spectrum (*m*/*z*) 255 (M+). Anal. ($C_{14}H_7NO_4$). C, H, N. (b) A mixture of hydroquinone-2,3-dicarboxylic *N*-phenylimide (2.55 g, 0.01 mol) in CCl_4 (20 mL) and phenyliodine ditrifluoroacetate (4.3 g, 0.01 mol) was stirred for 1 h. Workup as described above gave PBI (**5**) (2.5 g, 97%): IR (Nujol) 1730, 1600 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 7.12 (s, 2 H), 7.02–7.70 (m, 5 H, phenyl); mass spectrum (*m*/*z*) 255 (M+).

General Procedure for Cycloadditions. A solution of PBA (**4**) or PBI (**5**) and a slight excess amount of cyclic diene or cyclic triene in various solvents was stirred until the orange color had faded away. The precipitates were filtered off and purified by recrystallization. The reaction conditions and the yields of the adducts for the cycloadditions are summarized in Table III. For new compounds, physical properties and spectral data are summarized as follows:

***endo*-Pentacyclo[8.2.1.0^{2,3}.0^{3,11}.0^{4,9}]tridec-6-ene-5,8-dione-4,9-dicarboxylic anhydride (6)**, mp 206 °C dec as yellow prisms: IR (Nujol) 1800, 1683 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 1.16 (d, *J* = 6.0 Hz, 2 H), 1.56 (m, 1 H), 1.70 (s, 2 H), 2.03 (bs, 1 H), 3.08 (s, 2 H), 6.88 (s, 2 H); mass spectrum (*m*/*z*) 270 (M$^+$). Anal. ($C_{15}H_{10}O_5$). C, H.

***endo*-Pentacyclo[8.2.1.0^{2,13}.0^{3,11}.0^{4,9}]tridec-6-ene-5,8-dione-4,9-dicarboxylic *N*-phenylimide (7)**, mp 218 °C dec as yellow prisms: IR (Nujol) 1725, 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, *J* = 4.0 Hz, 2 H), 1.50 (m, 1 H), 1.57 (s, 2 H), 2.00 (bs, 1 H), 3.10 (bs, 2 H), 6.38 (s, 2 H), 7.20–7.50 (m, 5 H); mass spectrum (*m*/*z*) 345 (M$^+$). Anal. ($C_{21}H_{15}NO_4$). C, H, N.

***exo*-Tetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-5,11-diene-4,7-dione-3,8-dicarboxylic anhydride (9)**, mp 245 °C dec as yellow prisms: IR (Nujol) 1800, 1683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 and 1.68 (AB-q, *J* = 12 Hz, 2 H), 2.68 (s, 2 H), 3.19 (m, 2 H), 6.19 (m, 2 H), 6.92 (s, 2 H); mass spectrum (*m*/*z*) 270 (M$^+$). Anal. ($C_{15}H_{10}O_5$). C, H.

***exo*-Tetracyclo[8.2.1.0^{2,9}.0^{3,8}]trideca-5,11-diene-4,7-dione-3,8-dicarboxylic *N*-phenylimide (10)**, mp 258 °C as yellow prisms: IR (Nujol) 1685, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (bs, 1 H), 1.59 (s, 1 H), 2.60 (s, 2 H), 3.32 (m, 2 H), 6.12 (m, 2 H), 6.89 (s, 2 H), 7.20–7.50 (m, 5 H); mass spectrum (*m*/*z*) 345 (M$^+$). Anal. ($C_{21}H_{15}NO_4$). C, H, N.

(21) Mukherjee, D.; Watts, C. R.; Houk, K. N. *J. Org. Chem.* **1978**, *43*, 817.

Table III. Reaction Conditions and Yields for Cycloadditions

addend	reagent	reaction conditions: solvents	°C	time	yields (%) of 1:1 adducts
norbornadiene	PBA	C_6H_6	80	20 min	97
		$CHCl_3$	60	20 min	90
		CH_3CN	40	20 min	94
	PBI	$CHCl_3$	60	40 min	90
	p-benzoquinone	$CHCl_3$	60	1 h	none
		C_6H_5Cl	110	1 h	none
quadricyclane	PBA	C_6H_6	r.t.	10 min	quantitative
	PBI	C_6H_6	r.t.	20 min	quantitative
	p-benzoquinone	C_6H_5Cl	110	17 h	75[a]
6,6-dimethylfulvene	PBA	$CHCl_3$	r.t.	10 min	quantitative
	PBI	$CHCl_3$	r.t.	10 min	quantitative
cycloheptatriene	PBA	$CHCl_3$	r.t.	30 min	quantitative
	PBI	$CHCl_3$	r.t.	30 min	quantitative
tropone	PBI	C_6H_5Cl	110	2 h	76
	p-benzoquinone	C_6H_5Cl	110	2 h	none

[a] See ref 17.

11-Isopropylidene-*endo*-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene-3,6-dione-2,7-dicarboxylic anhydride (11), mp 147 °C dec as yellow prisms: IR (Nujol) 1800, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64 (s, 6 H), 4.42 (m, 2 H), 6.42 (dd, J = 2.0, 1.0, 2 H), 6.76 (s, 2 H); mass spectrum (m/z) 284 (M^+). Anal. ($C_{16}H_{12}O_5$). C, H.

11-Isopropylidene-*endo*-tricyclo[6.2.1.$0^{2,7}$]undeca-4,9-diene-3,6-dione-2,7-dicarboxylic *N*-phenylimide (12), mp 214 °C dec as yellow prisms: IR (Nujol) 1735, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (s, 6 H), 4.40 (m, 2 H), 6.42 (m, 2 H), 6.68 (s, 2 H), 7.02–7.45 (m, 5 H); mass spectrum (m/z) 359 (M^+). Anal. ($C_{22}H_{17}NO_4$). C, H, N.

***endo*-Tetracyclo[6.3.2.$0^{2,7}0^{9,11}$]trideca-4,12-diene-3,6-dione-2,7-dicarboxylic anhydride (15)**, mp 165 °C dec as yellow prisms: IR (Nujol) 1795, 1683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (m, 1 H), 0.42 (m, 1 H), 1.30 (m, 2 H), 4.10 (m, 2 H), 5.92 (dd, J = 4.0, 3.0 Hz, 2 H), 6.82 (s, 2 H); mass spectrum (m/z) 270 (M^+). Anal. ($C_{15}H_{10}O_5$). C, H.

***endo*-Tetracyclo[6.3.2.$0^{2,7}0^{9,11}$]trideca-4,12-diene-3,6-dione-2,7-dicarboxylic *N*-phenylimide (16)**, mp 210 °C as yellow prisms: IR (Nujol) 1725, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (m, 1 H), 0.35 (m, 1 H), 1.25 (m, 2 H), 4.15 (m, 2 H), 5.85 (dd, J = 8.5, 3.5 Hz, 2 H), 6.80 (s, 2 H), 7.00–7.50 (m, 5 H); mass spectrum 345 (M^+). Anal. ($C_{21}H_{15}NO_4$). C, H, N.

***exo*-Tricyclo[6.3.2.$0^{2,7}$]trideca-4,9,12-triene-3,6,11-trione-2,7-dicarboxylic *N*-phenylimide (19)**, mp 205 °C as pale yellow prisms: IR (Nujol) 1660, 1680, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.30 (dd, J = 8.0, 7.0 Hz, 1 H), 4.45 (d, J = 7.5, 1 H), 5.76 (dd, J = 11.0, 1.8 Hz, 1 H), 6.44 (t, J = 8.0, 7.5 Hz, 1 H), 6.76 (t, J = 8.0, 7.0 Hz, 1 H), 7.02 (s, 1 H), 7.04 (s, 1 H), 7.10 (q, J = 11.0, 8.0 Hz, 1 H), 7.08–7.60 (m, 5 H); mass spectrum (m/z) 359 (M^+). Anal. ($C_{21}H_{13}NO_5$). C, H, N.

Bromination of Compound 6. To a solution of **6** (1.0 g, 3.7 mmol) in acetic acid (10 mL) was added dropwise bromine (0.59 g, 3.7 mmol). The mixture was poured into water and the precipitated solids were filtered off and then recrystallized from $CHCl_3$ to give 6,7-dibromo-*endo*-pentacyclo[8.2.1.$0^{2,13}0^{3,11}0^{4,9}$]trideca-5,8-dione-4,9-dicarboxylic anhydride (**8**) (1.15 g, 72%), mp 146 °C dec as pale yellow prisms; ^1H NMR ($CDCl_3$) δ 1.40 (m, 2 H), 1.64 (m, 1 H), 1.72 (s, 2 H), 1.99 (bs, 1 H), 3.04 (m, 2 H), 2.68 and 2.83 (AB-q, J = 3.0, 2 H). Anal. ($C_{15}H_{10}O_5Br_2$). C, H.

General Procedure for Photochemical Reaction of the Adduct. A solution of the adduct in various solvents was irradiated several times with a 100-W high-pressure mercury lamp fitted with an I_2–CCl_4 filter solution under nitrogen at room temperature. After the consumption of starting materials was confirmed by UV spectrometer, the solvent was removed under reduced pressure at room temperature. The residual solids were chromatographed on a silica gel column by using various solvent mixtures. The ^1H NMR and characteristic carbonyl absorptions by IR are summarized in Table II. For new cage compounds, physical properties and the yields are summarized as follows:

13: mp 200 °C (sealed tube), as colorless prisms, yield 90%; mass spectrum (m/z) 284 (M^+). Anal. ($C_{16}H_{12}O_5 \cdot H_2O$). C, H.

14: mp 305 °C dec (sealed tube), as colorless prisms, yield 96%; mass spectrum 359 (M^+). Anal. ($C_{22}H_{17}O_4$). C, H.

17: mp 208 °C dec (sealed tube) as colorless prisms, yield 90%; mass spectrum (m/z) 270 (M^+). Anal. ($C_{15}H_{10}O_5 \cdot 2H_2O$). C, H.

18: mp 280 °C dec (sealed tube) as colorless prism, yield 94%; mass spectrum 345 (M^+). Anal. ($C_{21}H_{15}NO_4 \cdot {}^1/_2H_2O$). C, H.

20: mp 164 °C (sealed tube) as colorless prisms, yield 90% (using solvent of MeOH), 92% (using solvent of CH_2Cl_2); mass spectrum 359 (M^+). Anal. ($C_{21}H_{13}NO_5 \cdot 2H_2O$. C, H, N.