Site-Selective Diels–Alder Reactions of 1,4,5,8-Naphthodiquinones with Anthracenes and Successively with Cyclopentadiene: Elelctronic Effects vs. Steric Effects

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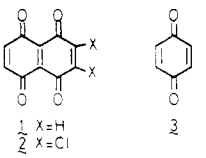
The cycloaddition reactions of naphthodiquinones with anthracene derivatives have been investigated. While anthracene (**4**) reacted with naphthodiquinones (**1**, **2**, and **13**) at the internal double bond to give the internal adducts (**6**, **7**, and **14**), the reaction of 9,10-substituted anthracenes (**5**) took place at the terminal double bond to afford the terminal adducts (**8**, **9**, and **15**). The successive reaction of adducts **6** and **7** with cyclopentadiene gave the Diels–Alder adducts **16** and **17**, respectively, which were photochemically converted into the cage compounds **18** and **19** in high yields. The reaction of **8** with cyclopentadiene afforded terminal adducts **20**, whereas the similar reaction of **9** gave internal adducts **21** which were smoothly converted on irradiation to the cage compounds **22**. The site selectivity in these reactions was discussed on the basis of the frontier molecular orbital (FMO) analysis as well as consideration of the steric effects of the substituents.

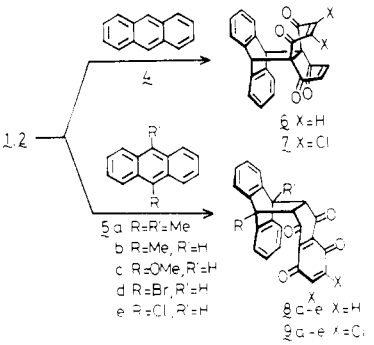
1,4,5,8-Naphthodiquinone (**1**) is a unique dienophile which is composed of two kinds of activated double bonds, i.e., the internal and terminal double bonds. Due to its markedly lowered LUMO energy level, **1** is a more powerful dienophile than the structurally related *p*-benzoquinone (**3**).[1,2] The frontier molecular orbital (FMO) considerations[3] of its Diels–Alder reactions suggest that the doubly activated internal double bond possessing the largest LUMO coefficients[2] will show the greater reactivity toward the electron-rich dienes than the singly activated terminal double bonds. However, it has been experimentally revealed that the cycloaddition reactions of naphthodiquinone and its derivatives with various dienes lead to variable results depending upon the dienes employed,[4-10] some of which are apparently opposed to the theoretical predictions. The origin of this intriguing site selection has not been fully understood and obviously more studies are needed in order to clarify the controlling factors in these pericyclic reactions of naphthodiquinones.

We have investigated the cycloaddition reactions of naphthodiquinones **1** and **2** with a series of substituted anthracenes and the Diels–Alder reactions of the resulting adducts with cyclopentadiene. It was found that the reaction site (site selectivity) in these successive Diels–Alder reactions was strongly influenced by the substituents both on the naphthodiquinones and the anthracenes. A reasonable explanation for this remarkable effect of substituents has been developed by evoking both electronic and steric factors. In addition, the Lewis-acid catalyzed cycloreversion as well as photochemical [2 + 2] cyclization of the adducts were also studied.

Chart I



Scheme I



Results and Discussion

Cycloaddition Reactions of Naphthodiquinones with Anthracenes. Previously, we reported that the reaction of naphthodiquinone **1** with anthracene (**4**) exclusively gave the adduct attached to the internal double bond (i.e., internal adduct) (**6**) in 75% yield.[2] It was now found that dichloronaphthodiquinone **2** similarly reacted with **4** in chloroform at room temperature under Ar to afford only the internal adduct **7** in 80% yield (Scheme I).

In sharp contrast, the reactions of **1** and **2** with 9-mono- or 9,10-disubstituted anthracenes **5a–e** under the same reaction conditions afforded in fair to excellent yields the Diels–Alder adducts formed at the terminal double bond (i.e., terminal adducts) **8a–e** and **9a–e**, respectively. No other type of adducts could be detected by the ^{1}H NMR analyses of the crude reaction mixtures. In the reaction of **5c**, however, a considerable amount of the reduction product (**11** or **12**) was also obtained (vide infra). The yields and the spectroscopic data of these adducts are summarized in Table I.

The structures of the adducts were unambiguously determined by the ^{1}H NMR spectra. For example, while the internal adduct **6** (or **7**) showed the signal of the methine protons (2 H) as a singlet at δ 5.53 (δ 5.55), the terminal adducts **8** displayed rather complicated pattern of signals

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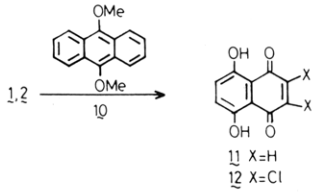
Table I. Yield and Spectral Data for Diels–Alder Adducts

no.	% yield[a]	mp,[b] °C	IR,[c] cm^{-1}	UV[e] max, nm (log ϵ)	^{1}H NMR,[f] δ (J, Hz)	MS, m/e
7	60	247–250	1710, 1680, 1580	251 sh (3.9), 269 sh (3.7), 360 (2.7), 380 (2.7), 416 sh (2.4)	7.03–7.35 (m, 8 H), 6.45 (s, 2 H), 5.53 (s, 2 H)	436 (M + 2), 434 (M$^+$), 258
8a	90	232–235	1720, 1705	254 (4.1), 352 (3.1)	7.10–7.38 (m, 8 H), 6.48 (s, 2 H), 3.00 (s, 2 H), 2.03 (s, 6 H)	394 (M$^+$), 206
8b	70	230–233	1715, 1705	266 sh (3.8), 275 sh (3.7), 351 (3.1)	7.08–7.36 (m, 8 H), 6.49 (s, 2 H), 4.67 (d, J = 3.0, 1 H), 3.33 (dd, J = 9.0, 3.0, 1 H), 2.90 (d, J = 9.0, 1 H), 2.02 (s, 3 H)	380 (M$^+$), 192
8c	38	230–233	1700, 1655	254 (4.3), 351 (3.2)	7.03–7.54 (m, 8 H), 6.50 (s, 2 H), 4.56 (d, J = 2.4, 1 H), 4, 12 (s, 3 H), 3.68 (d, J = 9.0, 1 H), 3.36 (dd, J = 9.0, 2.4, 1 H)	396 (M$^+$), 208, 193
8d	49	242–244	1710, 1665[d]	253 (4.1), 349 (3.0)	7.10–7.43 (m, 8 H), 6.52 (s, 2 H), 4.72 (m, 1 H), 3.39 (m, 2 H)	446 (M + 2), 444 (M$^+$)
8e	62	243–245	1700, 1650	264 (4.1), 345 (3.0)	7.11–7.41 (m, 8 H), 6.52 (s, 2 H), 4.70 (d, 1 H), 3.35 (m, 2 H)	402 (M + 2), 400 (M$^+$)
9a	64	185–188	1720, 1675, 1580	265 (4.0), 273 sh (4.0), 350 (3.4)	7.12–7.39 (m, 8 H), 3.03 (s, 2 H), 2.03 (s, 6 H)	464 (M + 2), 462 (M$^+$)
9b	69	209–211	1720, 1675,[d] 1565	267 (4.0), 276 sh (4.0), 351 (3.4)	7.11–7.36 (m, 8 H), 4.69 (d, J = 2.4, 1H), 3.38 (dd, J = 8.4, 2.4, 1 H), 2.93 (d, J = 8.4, 1 H), 2.03 (s, 3 H)	448 (M + 2), 446 (M$^+$)
9c	78	219–221	1720, 1675,[d] 1565		7.06–7.52 (m, 8 H), 3.69 (d, J = 9.0, 1 H), 3.39 (dd, J = 9.0, 2.4, 1 H)	446 (M + 2), 444 (M$^+$)
9d	57	215–217	1720, 1575		7.13–7.40 (m, 8 H), 4.74 (d, 1 H), 3.43 (m, 2 H)	516 (M + 4), 514 (M + 2), 512 (M$^+$)
9e	20	200–202	1720, 1560	251 (4.0), 349 (3.2)	7.14–7.48 (m, 8 H), 4.73 (d, 1 H), 3.37 (m, 2 H)	472 (M + 4), 470 (M + 2), 468 (M$^+$)

[a] All isolated yields. [b] All compounds decomposed at their melting points. [c] Nujol. [d] $CHCl_3$. [e] $CHCl_3$, sh = shoulder. [f] $CDCl_3$.

for the methine protons (2 H or 3 H depending on R and R′) together with a characteristic sharp singlet of the enedione olefin protons (2 H) at δ 6.5. In the case of adducts **9**, the absence of signals attributable to the enedione moiety indicated that the cycloaddition reaction of **2** took place at the unsubstituted terminal double bond.

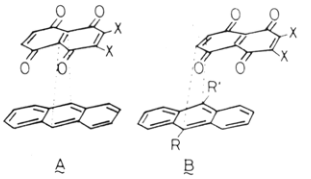
The reactions of **1** and **2** with electron-deficient anthracenes such as 9-anthraldehyde and 9-cyanoanthracene under the same reaction conditions failed, and the starting materials were recovered unchanged. Interestingly, treatment of **1** with a strongly electron-rich anthracene like 9,10-dimethoxyanthracene (**10**) in chloroform (room temperature, Ar) led to the smooth formation of the reduction product **11** and recovery of unchanged **10** (eq 1).[11] Similarly, the reaction of **2** with **10** in chloroform[11] afforded only **12** in a high yield. The control experiment showed that compound **1** (or **2**) without **10** was fairly stable in chloroform and only a slight formation of **11** (or **12**) was observed after a prolonged time. This suggests that reduction of **1** (or **2**) may occur via an electron transfer from the electron-rich anthracenes such as **5c** and **10** to electron-deficient **1** or **2**.



(1)

Site Selectivity. The above results show a remarkable site selectivity in cycloaddition of **1** and **2** with anthracene derivatives. While anthracene itself reacted with diquinones (**1** and **2**) at the internal double bond, the substituted anthracenes added to the unsubstituted terminal double bond. This site selection can be reasonably explained by the FMO theory as well as consideration of the steric factors. In the absence of the steric obstruction at the 9,10-positions of anthracene, the reaction would take place predominantly at the doubly activated internal double bond of **1** (or **2**) via a transition state with the maximum p orbital overlap (A, Chart II) as anticipated by the FMO considerations.[2,3] However, in the case of substituted anthracenes like **5a–e**, the severe steric hindrance at the 9,10-positions would prevent this face-to-face approach and instead favor the reaction at the terminal double bond via a sterically less hindered transition state (B, Chart II).

Chart II



In order to evaluate the importance of donor–acceptor interaction[12,13] in these cycloaddition reactions and its effect on the site selectivity, we have investigated the reactions of 2-methoxynaphthodiquinone (**13**) which was shown to possess the higher LUMO energy level compared with those of **1** and **2** by the CNDO/2 MO calculations.[14] While the reaction of **13** with anthracene (**4**) afforded only internal adduct **14** (98%), the reaction with dimethyl-

(11) Since no reduction of **1** and **2** occurred in benzene even in the presence of **10**, the acid present in chloroform seems to be also needed for this reductive transformation.

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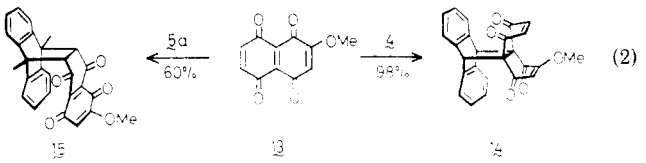
(14) The MO calculations by CNDO/2 method showed the following LUMO energy levels: **1** (−0.9539 eV), **2** (−1.4487 eV), and **13** (−0.8873 eV).

Table II. Spectral Data for Adducts

no.	^{1}H NMR,[a] δ (J, Hz)	IR (Nujol), cm^{-1}	MS, m/e
16	7.01–7.44 (m, 8 H), 6.32 (s, 2 H), 5.88 (dd, J = 1.8, 2 H), 5.23 (s, 2 H), 3.25 (m, 2 H), 2.41 (dd, J = 2.2, 1.5, 2 H), 1.26 (dm, J = 8.9, 1 H), 1.01 (dm, J = 8.9 1 H)	1715	432 (M$^+$), 254, 178
17	7.01–7.40 (m, 8 H), 5.90 (m, 2 H), 5.24 (s, 2 H), 3.28 (m, 2 H), 2.37 (m, 2 H), 1.83 (dm, J = 10.0, 1 H), 1.47 (dm, J = 10.0, 1 H)	1715, 1580	502 (M + 2), 500 (M$^+$), 178
18	7.29–7.40, 6.97–7.10 (m, 8 H), 5.52 (s, 2 H), 3.23–3.32 (m, 4 H), 2.98 (m, 4 H), 1.66 (dm, J = 9.6, 1 H), 1.43 (dm, J = 9.6, 1 H)	1715, 1690	432 (M$^+$), 298, 178
19	7.32–7.44, 6.97–7.11 (m, 8 H), 5.64 (s, 2 H), 3.55 (m, 2 H), 3.03 (m, 4 H), 1.33 (dm, J = 9.0, 1 H), 0.95 (dm, J = 9.0, 1 H)	1735, 1700	502 (M + 2), 500 (M$^+$), 178
20a	7.12–7.35 (m, 8 H), 5.93 (m, 2 H), 3.39 (m, J = 2.0, 2 H), 2.94 (d, J = 2.0, 2 H), 2.91 (s, 2 H), 2.01 (s, 6 H), 1.46 (dm, J = 8.5, 1 H), 1.28 (dm, J = 8.5, 1 H)	1715, 1680	394, 254, 206
20b	7.11–7.35 (m, 8 H), 5.93 (m, 2 H), 4.46 (d, J = 2.8, 1 H), 3.39 (m, J = 1.7, 2 H), 3.25 (dd, J = 8.8, 2.8, 1 H), 2.95 (m, 2 H), 2.82 (d, J = 8.8, 1 H), 2.01 (s, 3 H), 1.46 (dm, J = 8.2, 1.7, 1 H), 1.29 (dm, J = 8.2, 1.7, 1 H)	1715, 1680	380, 192
21a	7.03–7.33 (m, 8 H), 6.02 (m, 2 H), 4.12 (m, 2 H), 3.09 (s, 2 H), 1.95 (s, 6 H), 1.30 (dm, J = 10.8, 1 H), 0.86 (dm, J = 10.8, 1 H)	1715, 1675, 1575	528 (M$^+$), 206, 191
21b	7.01–7.31 (m, 8 H), 6.04 (m, 2 H), 4.59 (d, J = 2.4, 1 H), 4.14 (m, 2 H), 3.37 (dd, J = 10.8, 2.4, 1 H), 2.98 (d, J = 10.8, 1 H), 1.94 (s, 3 H), 1.30 (dm, J = 11.4, 1 H), 0.87 (dm, J = 11.4, 1 H)	1715, 1680, 1575	514 (M$^+$), 192
22a	6.99–7.46 (m, 8 H), 3.65 (m, 2 H), 3.24 (m, 2 H), 2.97 (s, 2 H), 2.20 (s, 6 H), 1.66 (bs, 2 H)	1780, 1765	530 (M + 2), 528 (M$^+$), 206
22b	6.99–7.50 (m, 8 H), 4.98 (d, J = 2.4, 1 H), 3.73 (m, 1 H), 3.53 (m, 1 H), 3.30 (m, 2 H), 3.21 (dd, J = 10.8, 2.4, 1 H), 2.85 (d, J = 10.8, 1 H), 2.18 (s, 3 H), 1.75 (bs, 2 H)	1785, 1770	516 (M + 2), 514 (M$^+$), 192

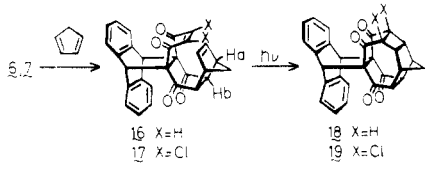
[a] $CDCl_3$.

anthracene (**5a**) gave terminal adduct **15** (60%) (eq 2). These results further indicate that the site selectivity in these cycloadditions is mainly controlled by the steric factors.



(2)

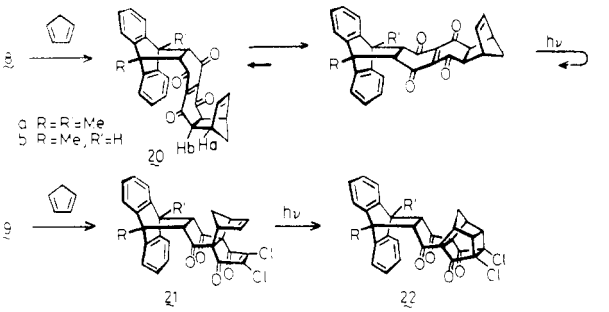
Cycloaddition Reactions of Internal Adducts. The internal adducts obtained above possess two enedione moieties in the longicyclic positions. This unique structural feature led us to investigate further Diels–Alder reactions with another diene compound. When **6** and **7** were treated with cyclopentadiene in methylene chloride at room temperature (20 h), crystalline adducts **16** and **17** were obtained in 64% and 60% yields, respectively (eq 3). The structural determination of these products was made on the basis of the spectroscopic data (Table II) as well as chemical transformations. In the ^{1}H NMR spectrum of **16**, the presence of appreciable coupling (J = 2.2 Hz) between two methine protons (Ha and Hb) was indicative of the endo stereochemistry, which was further confirmed by the smooth [2 + 2] photocyclization (vide infra). In the case of **17**, the absence of the characteristic signals for enedione olefinic protons indicated that the addition took place at the unsubstituted double bond of **7**. The mass spectrum of **16** displayed a weak molecular ion peak at m/e 432 (0.1%) but intense fragment peaks at m/e 254 (100%) and 178 (80%), suggesting an easy retro-Diels–Alder fragmentation of the anthracene moiety from adduct **16**.



(3)

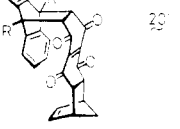
Irradiation of adducts **16** and **17** in chloroform with a 400-W high-pressure mercury lamp through a Pyrex filter resulted in the smooth formation of cage compounds **18** and **19**, respectively (eq 3). In these products, the ring formation by [2 + 2] cycloaddition between cyclopentene and enedione double bonds was apparent from the ^{1}H NMR spectra (Table II), which were characterized by the absence of olefinic proton signals. In contrast to **16** and **17**, the mass spectra of these photoproducts showed rather intense molecular ion peaks.

Scheme II



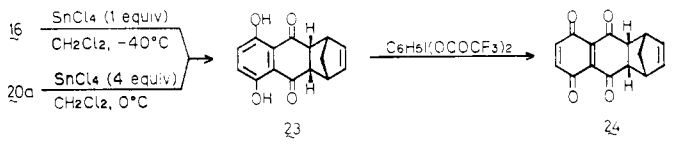
Cycloaddition Reactions of Terminal Adducts. Since the terminal adducts **8** and **9** contain two different kinds of enedione moieties, it is of interest to study which double bond is responsible for the next cycloaddition reactions. Thus, treatment of **8a,b** with cyclopentadiene in methylene chloride at room temperature (20 h) exclusively gave the adducts at the terminal double bond, **20a,b**, in 77% and 66% yields, respectively. In sharp contrast, the similar reactions of **9a,b** afforded only the adducts at the internal double bond, **21a,b**, in 80–90% yields (Scheme II).

The structural assignments of these products were made on the basis of elemental analyses, spectroscopic data (Table II), and chemical transformations. The gross structure of **20** was determined by the careful analysis of



^{1}H NMR spectra (Table II) as well as spin-decoupling experiments. The observation of coupling (J = 2.0 Hz for **20a**) between Ha and Hb suggested the endo configuration with respect to the norbornene moiety as shown in **20**. The structure of **20** was further confirmed by converting to **23** via Lewis acid catalyzed cycloreversion (vide infra),

Scheme III



whereas compounds **20** were photochemically inactive and recovered unchanged even after a prolonged irradiation. This presumably reflects the conformational preference of **20** for the "extended" form rather than the "folded" form.[24] While these spectral data and chemical transformations cannot fully rule out the alternative structure **20′**, its formation seems to be sterically less favorable. On the other hand, for the structural elucidation of **21** IR spectra were very instructive. A characteristic absorption band at 1580 cm^{-1} was indicative of the presence of a dichlorinated double bond in **21**.[15] The endo stereochemistry of **21** was nicely revealed by the following photochemical [2 + 2] cycloaddition. Thus, brief irradiation of **21a,b** in chloroform solution afforded almost quantitative yields of the cage compounds **22a,b** (Scheme II). IR spectra of these photoproducts showed no absorption bands near 1580 cm^{-1}.

It is of interest to note that the cycloaddition of **8** with cyclopentadiene occurred at the singly activated terminal double bond rather than the doubly activated internal double bond, while **9** reacted with the latter double bond. This indicates that the reactivity of the internal double bond in **8** may be somewhat decreased compared with the terminal double bond probably due to the electron donation of the proximate aromatic ring.[16] It should also be noted that these results show a general tendency to avoid reaction at the dichloroenedione double bonds (**1**, **2** → **8**, **9**, and **9** → **21**).

Lewis Acid Catalyzed Cycloreversion Reactions. In order to explore the utility of anthracenes as a protecting group and/or directing group[17,18] of naphthodiquinones, cycloreversion reaction of the above adducts was briefly investigated. Although the thermolysis of **16** in toluene at 80–120 °C gave a mixture of several minor products, treatment of **16** with 1 equiv of $SnCl_4$ in methylene chloride at −40 °C (30 min) resulted in a smooth cycloreversion to give **23** (and anthracene) in quantitative yield (Scheme III). Adduct **20a** also gave **23** in a high yield on treatment with $SnCl_4$ (4 equiv) at 0 °C. Compound **23** was identical in all aspects with an authentic sample prepared by the direct reaction of **11** with cyclopentadiene. In contrast, cage compounds **18** and **22** and adduct **21** were stable under the similar Lewis acid treatment, suggesting a necessity for the enedione moiety for a facile cycloreversion reaction. Use of a large excess of Lewis acid and/or treatment at the higher temperature only led to a complex mixture of products. Oxidation of **23** with [bis(trifluoroacetoxy)-iodo]benzene[19] afforded **24**, the formal terminal adduct of **1** with cyclopentadiene (Scheme III) which could not be obtained by their direct reaction.[2]

In conclusion, the cycloaddition reactions of naphthodiquinones (**1**, **2**, and **13**) with various anthracene derivatives show a remarkable site selectivity which is controlled by rather delicately balanced steric and electronic factors. In the reaction of 9-(or 10-)substituted anthracenes, the steric factor seems to play the major role for this site selection.

Experimental Section

The melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. The UV spectra were determined with a Shimadzu UV-260 spectrophotometer. The ^1H NMR spectra were taken with a JEOL PS-100 spectrometer and a Hitachi R-600 spectrometer with tetramethylsilane as an internal standard, and the chemical shifts are expressed in δ values. The ^{13}C NMR spectra were determined with a JEOL-100 with tetramethylsilane as an internal standard. The IR spectra were taken with a JASCO IR A-100 infrared spectrophotometer. Mass spectra were determined with a JEOL-01SG double-focusing spectrometer operated 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. Column chromatography was performed by using E. M. Merck kieselgel 60 (70–200) mesh.

Materials. All solvents were reagent grade (Nakarai) and were used as received unless otherwise noted. 1,4,5,8-Naphthodiquinone (NDQ) (**1**),[2] 2,3-dichloronaphthodiquinone (DNDQ) (**2**),[2] and methoxyanthracene **5c**[20] were prepared according to the reported methods. Dimethoxyanthracene **13** was prepared by the modified method.[21] All other anthracene derivatives were commercially available.

General Procedure for Cycloaddition Reactions of Naphthodiquinones (1 and 2) with Anthracenes. A solution of NDQ (**1**) or DNDQ (**2**) and 1 equiv of appropriate anthracene derivative (**4** or **5a–e**) in dry benzene or dry chloroform was stirred under Ar at room temperature. The reaction was monitored by TLC. When the starting materials were consumed (5–48 h), the precipitates were collected by filtration and analyzed by ^1H NMR spectroscopy. Since the products decomposed on silica gel, purification was carried out by recrystallization from chloroform to give pure adducts. The yields, physical properties, and spectral data of adducts are summarized in Table I.

Reaction of Naphthodiquinone (1) with 9,10-Dimethoxyanthracene (10). A suspension of **1** (120 mg, 0.64 mmol) and **10** (152 mg, 0.64 mmol) in dry chloroform (20 mL) was stirred for 3 h under Ar at room temperature. The resulting solution was evaporated in vacuo and the residual solids were chromatographed on a silica gel column with *n*-hexane/ethyl acetate (4:1) to give **11** (100 mg, 88%) as red crystals which were identical with an authentic sample[22] by TLC, IR, and NMR.

Reaction of Dichloronaphthodiquinone (2) with 9,10-Dimethoxyanthracene (10). A similar reaction of DNDQ (**2**) (134 mg, 0.52 mmol) with **10** (259 mg, 1.09 mmol) followed by the same workup as above afforded dichloronaphthazarin **12**[23] (120 mg, 89%) as red crystals.

Methoxynaphthodiquinone (13). A solution of **11** (5 g, 26.3 mmol) in 1.2 L of water containing 35 mL of 6 N sodium hydroxide solution was refluxed for 4 h on an oil bath with a rapid stream of air passing through the solution. After cooling, the solution was just acidified with acetic acid and filtered. The filtrate was evaporated in vacuo, and the residual solids were dried in a vacuum oven at 60 °C. After addition of methanol (200 mL), the resulting suspension was stirred under bubbling dry hydrogen chloride for 3–4 h. The precipitates were filtered off and the filtrate was condensed under reduced pressure. The residue was chromatographed on a silica gel column with *n*-hexane/ethyl acetate (2:1) to give methoxynaphthazarin (450 mg, 18%): mp 188–190 °C; ^1H NMR ($CDCl_3$) δ 12.64 (s, 1 H), 12.18 (s, 1 H), 7.25 (s, 2 H), 3.94 (s, 3 H); IR ($CHCl_3$) 3520, 1720, 1595 cm^{-1}.

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A mixture of methoxyanphthazarin (350 mg, 1.61 mmol) and [bis(trifluoroacetoxy)iodo]benzene (1.04 g, 2.42 mmol) in 8 mL of acetone was stirred for 1 h at room temperature. The precipitates were collected by filtration and recrystallized from benzene to give **13** (140 mg, 40%) as orange crystals: mp 195–197 °C; ^{1}H NMR ($CDCl_3$) δ 6.85 (s, 2 H), 6.07 (s, 1 H), 3.87 (s, 3 H); IR ($CHCl_3$) 1705, 1685 cm^{-1}.

Reaction of Methoxynaphthodiquinone (13) with Anthracene (4). A suspension of **13** (36 mg, 0.17 mmol) and **4** (30 mg, 0.17 mmol) in dry chloroform (5 mL) was stirred under Ar at room temperature. After the consumption of the starting materials, the precipitates were collected by filtration and analyzed by ^{1}H NMR spectroscopy. Recrystallization from chloroform gave pure **14** (65 mg, 98%) as yellow crystals: mp 212–214 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.01–7.40 (m, 8 H), 6.45 (s, 2 H), 5.74 (s, 1 H), 5.58 (s, 2 H), 3.56 (s, 3 H); IR ($CHCl_3$) 1690 cm^{-1}; MS, *m/e* 396 (M^+).

Reaction of Methoxynaphthodiquinone (13) with Dimethylanthracene (5). A similar reaction of **13** (85 mg, 0.40 mmol) with **5** (82 mg, 0.40 mmol) in chloroform followed by the same workup as above afforded **15** (100 mg, 60%) as orange crystals: mp 177–179 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.10–7.37 (m, 8 H), 5.67 (s, 1 H), 3.74 (s, 3 H), 2.98 (s, 2 H), 2.03 (s, 6 H); IR ($CHCl_3$) 1705 cm^{-1}; MS, *m/e* 220 (methoxynaphthazarin).

General Procedure for Cycloaddition Reactions of the Adducts 6–9 with Cyclopentadiene. A solution of appropriate adduct (**6–9**) and an excess of cyclopentadiene (2 equiv) in dry chloroform or dry methylene chloride was stirred under Ar at room temperature. The reaction was monitored by TLC. After the starting materials **6–9** completely disappeared, the solution was evaporated in vacuo, and the residual solids were purified by recrystallization from chloroform to give pure products as follows.

16: 64%; mp 179 °C dec. Anal. Calcd for $C_{29}H_{20}O_4$: C, 80.54; H, 4.66. Found: C, 80.51; H, 4.69.

17: 60%; mp 185–188 °C dec. Anal. Calcd for $C_{29}H_{18}O_4Cl_2$: C, 69.47; H, 3.62. Found: C, 69.46; H, 3.66.

20a: 77%; mp 242–244 °C dec. Anal. Calcd for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25. Found: C, 80.83; H, 5.27.

20b: 66%; mp 230–235 °C dec.

21a: 87%; mp 175–178 °C dec. Anal. Calcd for $C_{31}H_{22}O_4Cl_2$: C, 70.33; H, 4.19. Found: C, 70.17; H, 4.34.

21b: 86%; mp 196–199 °C dec. Anal. Calcd for $C_{30}H_{20}O_4Cl_2$: C, 69.91; H, 3.91. Found: C, 69.82; H, 3.94.

The spectroscopic data for these products are summarized in Table II.

General Procedure for Photochemical Reactions of Adducts 16, 17, 20, and 21. A solution of the appropriate adduct in chloroform was irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter at room temperature. The reaction was monitered by TLC and ^{1}H NMR spectroscopy. After the starting material was completely consumed, the solution was evaporated in vacuo, and the residual solids were purified by recrystallization from chloroform to afford pure products as follows.

18: 100%; mp >300 °C.

19: 100%; mp >300 °C. Anal. Calcd for $C_{29}H_{18}O_4Cl_2$: C, 69.47; H, 3.62. Found: C, 69.71; H, 3.38.

22a: 100%; mp 185–190 °C dec. Anal. Calcd for $C_{31}H_{22}O_4Cl_2$: C, 70.33; H, 4.19. Found: C, 70.39; H, 4.14.

22b: 100%; mp 188–191 °C dec.

The spectroscopic data of these photoproducts are given in Table II.

Lewis Acid Catalyzed Cycloreversion of 16. A solution of **16** (10 mg, 0.027 mmol) and $SnCl_4$ (3.1×10^{-3} mL, 0.027 mmol) in dry methylene chloride (5 mL) was stirred under Ar at −40 °C. The reaction was monitored by TLC. After the consumption of the starting material, the reaction mixture was quenched with 5 mL of H_2O/THF (1:1). The organic layers were repeatedly extracted with methylene chloride, washed with brine, dried over Na_2SO_4, and evaporated in vacuo. The residual solids were chromatographed on a silica gel column with *n*-hexane/ethyl acetate (5:1) to give **20** (6 mg, 87%) as yellow crystals: mp 135–138 °C dec; ^{1}H NMR ($CDCl_3$) δ 12.61 (s, 2 H), 7.20 (s, 2 H), 6.07 (m, 2 H), 3.68 (m, 2 H), 3.42 (m, 2 H), 1.56 (s, 2 H); IR ($CHCl_3$) 1635 cm^{-1}; MS, *m/e* 256 (M^+).

Lewis Acid Catalyzed Cycloreversion of 20a. A similar reaction of **20a** (50 mg, 0.11 mmol) and $SnCl_4$ (0.065 mL, 0.55 mmol) in dry methylene chloride (10 mL) at −40 °C gave **23** (16 mg, 57%).

1,4,4a,9a-Tetrahydro-5,8-dihydroxy-1,4-methano-9,10-anthraquinone (23). To a solution of **11** (100 mg, 0.52 mmol) in methylene chloride (2 mL) was added cyclopentadiene (68.6 mg, 1.04 mmol) and the resulting solution was stirred at room temperature for 30 min. The reaction mixture was evaporated in vacuo and the residual solids were chromatographed on a silica gel column with *n*-hexane/ethyl acetate (6:1) to give **23** (135 mg, 100%) which was identical with the above obtained **23** by TLC, IR, and NMR.

5,5a,8,8a-Tetrahydro-5,8-methano-1,4,9,10-anthradiquinone (24). A mixture of **23** (400 mg, 1.56 mmol) and [bis(trifluoroacetoxy)iodo]benzene (1.01 g, 2.34 mmol) in 8 mL of acetone was stirred at room temperature for 1 h. The solution was concentrated under the reduced pressure to give the precipitates which were collected by filtration. Recrystallization from benzene gave **24** (230 mg, 58%) as red crystals: mp 161–163 °C dec; ^{1}H NMR ($CDCl_3$) δ 6.78 (s, 2 H), 6.11 (m, 2 H), 3.55 (m, 2 H), 3.48 (m, 2 H), 1.67 (dm, J = 8.4 Hz, 1 H), 1.45 (dm, J = 8.4 Hz, 1 H); IR ($CHCl_3$) 1700 cm^{-1}; MS, *m/e* 254 (M^+).

Registry No. **1**, 23077-93-2; **2**, 78456-63-0; **4**, 120-12-7; **5a**, 781-43-1; **5b**, 779-02-2; **5c**, 2395-96-2; **5d**, 1564-64-3; **5e**, 716-53-0; **6**, 78456-66-3; **7**, 96166-07-3; **8a**, 96166-08-4; **8b**, 96166-09-5; **8c**, 96166-10-8; **8d**, 96166-11-9; **8e**, 96166-12-0; **9a**, 96166-13-1; **9b**, 96166-14-2; **9c**, 96166-15-3; **9d**, 96166-16-4; **9e**, 96166-17-5; **10**, 2395-97-3; **11**, 475-38-7; **12**, 14918-69-5; **13**, 96166-06-2; **14**, 96193-99-6; **15**, 96194-10-4; **16**, 96194-00-2; **17**, 96194-01-3; **21a**, 96194-02-4; **21b**, 96194-03-5; **18**, 96194-04-6; **19**, 96194-05-7; **20a**, 96194-06-8; **20b**, 96194-07-9; **22a**, 96194-08-0; **22b**, 96194-09-1; **23**, 96243-32-2; **36**, 96166-18-6; methoxynaphthazarin, 14918-66-2; 1,3-cyclopentadiene, 542-92-7.