Table V. Neutral Hydrolysis of 1 and 3 in 1,4-Dioxane–H_2O and *t*-BuOH–H_2O at 25 °C

compd	solvent	n_{H_2O}	ϵ	k_w/k_{obsd}
1	H_2O	1.00	78.6	1
1	1,4-dioxane–H_2O	0.95	60.8	2.54
1	1,4-dioxane–H_2O	0.92	52	5.13
3	1,4-dioxane–H_2O	0.95	60.8	2.54
3	1,4-dioxane–H_2O	0.92	52	4.92
1	*t*-BuOH–H_2O	0.95	65.4	2.36
1	*t*-BuOH–H_2O	0.92	58.1	4.35
1	*t*-BuOH–H_2O	0.90	53.5	5.69
3	*t*-BuOH–H_2O	0.95	65.4	3.67
3	*t*-BuOH–H_2O	0.92	58.1	7.52
3	*t*-BuOH–H_2O	0.90	53.5	13.60

Table VI. Pseudo-First-Order Rate Constants ($10^4 k_{obsd}$, s^{-1}) for the Neutral Hydrolysis of 3 in Aqueous Solutions Containing SDS and *N*-Isopropylpyrrolidone at 25 °C

	[*N*-*i*-PP], M				
SDS, M	0.00	0.02	0.03	0.04	0.05
0.010	2.94	2.99	3.02	3.06	3.13
0.015	1.59	1.70	1.83	1.88	1.92
0.020	1.22	1.33	1.44	1.49	1.54

celles is caused by a larger initial-state stabilization effect as a result of stronger hydrophobic interactions. This explanation holds even if both substrates are bound at the same binding sites in the (mixed) micelles. Therefore, we emphasize that the different inhibition observed for **1** and **3** does not necessarily imply different binding sites or different orientational effects.

Addition of *N*-isopropylpyrrolidone (*N*-*i*-PP, the model monomer unit of PVP) to SDS solutions causes an increase in k_{obsd} for hydrolysis of **3** compared to the k_{obsd} values in the corresponding SDS solutions (Table VI). As shown by previous ultrafiltration measurements,[4] competition in binding between *N*-*i*-PP and **3** to the micelle will lead to transfer of **3** from the micellar pseudophase to the bulk aqueous phase and a concomitant increase in rate. In this respect the kinetic effect of the monomer is fundamentally different from that of the polymer.

Experimental Section

Materials. 1-Benzoyl-1,2,4-triazole (**1**, mp 72.1–72.5 °C (lit.[10a] mp 71.8–72.4 °C)), 1-phenacyl-1,2,4-triazole (**2**, mp 114.4–115.0 °C (lit.[10a] mp 114.0–115.2 °C)), and 3-phenyl-1-benzoyl-1,2,4-triazole (**3**, mp 79.1–79.5 °C (lit.[10a] mp 78.6–79.9 °C)) were prepared by literature methods.[10] SDS was purified by a standard method.[16] *N*-Isopropylpyrrolidone (GAF corporation, New York) was distilled twice under reduced pressure (bp 59 °C (0.001 mm)). The purification of poly(*N*-vinylpyrrolidone) (Kolloidon-90, BASF) has been described previously.[4] The copolymers poly(vinyl acetate)-poly(vinyl alcohol) Mowiol 3-83 (17% acetate) and Mowiol 10-74 (26% acetate) (both from Hoechst) were first fractionated from DMF–ether. Aqueous solutions (5%, w/w) of these materials were deionized by passing through cationic (Dowex-50w) and anionic (Dowex-1) ion exchange columns till the specific conductivities of the solutions were less than 20 μohm^{-1} cm^{-1}. The deionized solutions were dialized against demineralized water in cellulose acetate tubes for 24 h. Then the solutions were freeze dried and the copolymers were finally dried over P_2O_5 in vacuo. Weight averaged molecular weights were 1.79×10^4 D for Mowiol 3-83 and 6.04×10^4 D for Mowiol 10-74.

Measurements. The kinetic, conductivity, and ultrafiltration measurements have been carried out as described previously.[4,7,10] Generally, the k_{obsd} values were reproducible to within 2%.

Acknowledgment. The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO). We thank J. J. Lukkien for writing the computer program and Dr. L. Dijkema for generously providing samples of the copolymers.

Registry No. 1, 60718-51-6; 3, 79746-00-2; SDS, 151-21-3; PVP (homopolymer), 9003-39-8; Mowiol 3-83, 9002-89-5; Mowiol 10-74, 9002-89-5.

Supplementary Material Available: Figure 5, showing a plot of the specific conductivity of SDS at a series of fixed concentrations of Mowiol 10-74 (1 page). Ordering information is given on any current masthead page.

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Photoinduced Electron-Transfer-Initiated Aromatic Cyclization

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Photochemical reaction of substituted 1,4-naphthoquinones with 1,1-diarylethylenes led primarily to benz[*a*]anthracene-7,12-dione derivatives. Evidence was obtained that the photoreaction proceeded via a photoinduced electron-transfer process. Extension of the reaction provided regioselective syntheses of other polycyclic aromatic quinones.

Polycyclic aromatic compounds have attracted much attention because of their physicochemical and biochemical properties.[1] However, investigations of polycyclic aromatic compounds have been hampered by lack of general and facile regioselective synthetic routes to them.[2] A facile route to A ring substituted benz[*a*]anthracene-7,12-diones was recently reported[3a] using the Diels–Alder reaction of 1,4-naphthoquinone with styrene derivatives. However, several weeks are required to complete the Diels–Alder

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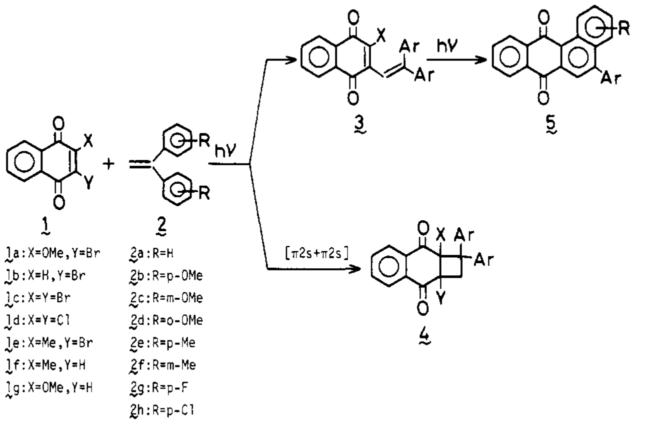
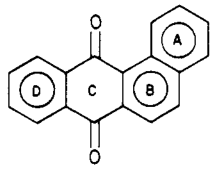
0022-3263/85/1950-0052$01.50/0

Scheme I. Photochemical Reactivity of Substituted 1,4-Naphthoquinone (1) with 1,1-Diarylethylene (2)



reaction even at high temperature. Moreover, the utility of this procedure is limited because of the difficulty of controlling regioselectivity when ring substituted 1,4-naphthoquinones are employed.[3b]



benz[a]anthracene-7,12-dione

Previously, we reported that benz[a]anthracene-7,12-dione derivatives are readily synthesized by photochemical reactions of 2,3-disubstituted 1,4-naphthoquinones with 1,1-diarylethylenes.[4] We now report mechanistic investigations[5] and extensions of the reaction.

Results and Discussion

In general, photochemical reactions[5] of substituted 1,4-naphthoquinones **1a–g** with 1,1-diarylethylenes **2a–h** produce ethylene adducts **3** and cyclobutane adducts **4** (Scheme I). Ethylene adduct **3a** was produced by the reaction of **1a** with **2a**. This adduct reacted further to give benz[a]anthracene-7,12-dione derivative **5a**. Two possible reaction pathways for formation of the ethylene adduct **3** are depicted in Scheme II. We show later that the path via cyclobutane **4** is not followed. The other path via electron transfer to produce an ion radical pair or exciplex seems likely because of the high electron-accepting character of 1[7] and the high electron-donating character of **2**.[8] This path is supported by our finding that the polarity of

Scheme II. Possible Reaction Mechanisms of Benz[a]anthracene-7,12-dione Derivative Formation

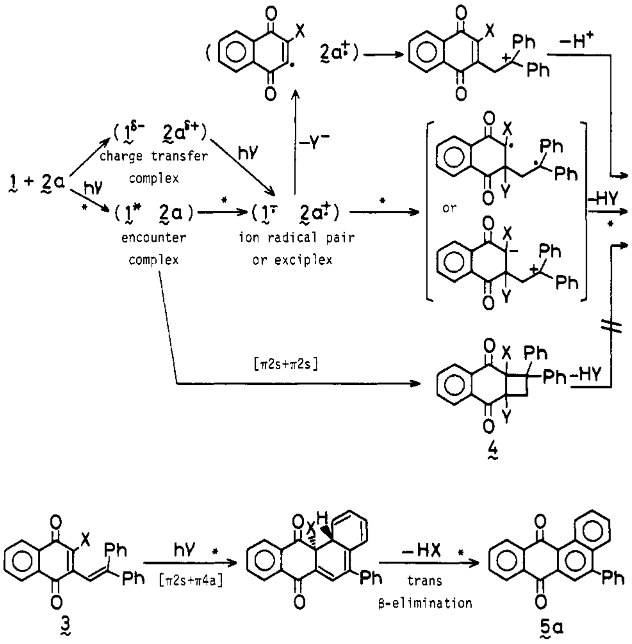
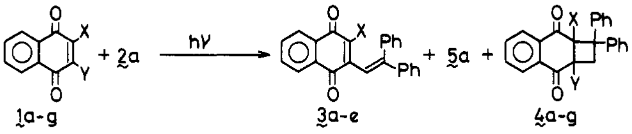


Table I. Photochemical Reactions of Substituted 1,4-Naphthoquinones (1a–g) with 1,1-Diphenylethylene (2a)



starting quinone	irradiation time, h[b]	products (yield %)[a]		
		3	5a	4
1a, X = OMe; Y = Br	11[c]	**3a**, X = OMe	(46)	**4a**, X = OMe; Y = Br (0)
1b, X = H; Y = Br	10[c]	**3b**, X = H	(26)	**4b**, X = H; Y = Br (0)
1c, X = Y = Br	100[d]	**3c**, X = Br (30)	(24)	**4c**, X = Y = Br (trace)
1d, X = Y = Cl	70[c]	**3d**, X = Cl	(25)	**4d**, X = Y = Cl (50)
1e, X = Me; Y = Br	6[e]	**3e**, X = Me (0)	(0)	**4e**, X = Me; Y = Br (41) **4e′**, X = Br; Y = Me (10)
1f, X = Me; Y = H	30[e]	**3e**, X = Me (0)	(0)	**4f**, X = Me; Y = H **4f′**, X = H; Y = Me (92) 1:2.5 mixture
1g, X = OMe; Y = H	4[e]	**3a**, X = OMe (0)	(0)	**4g**, X = OMe; Y = H (94)

[a] Isolated yields based on starting quinone 1. [b] Irradiation was carried out in a benzene solution (25 mL) of **1** (1 mmol), **2a** (2 mmol), and pyridine (2 mmol). [c] Irradiation was continued until complete consumption of the ethylene adduct was shown by TLC. [d] Further photoreaction of **3c** into **5a** was very slow so that irradiation was stopped after 100 h. [e] Irradiation was continued until complete consumption of the starting quinone was shown by TLC.

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(4) (a) Maruyama, K.; Otsuki, T. *Chem. Lett.* **1975**, 87. (b) Maruyama, K.; Otsuki, T.; Mitsui, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3361. (c) Maruyama, K.; Otsuki, T.; Mitsui, K. *J. Org. Chem.* **1980**, *45*, 1424.

(5) Neither fluorescence spectra of substituted 1,4-naphthoquinones nor exciplex emission spectra in a mixture of quinone and 1,1-diarylethylene could be observed. It is known[6] that subsequent chemical reaction of excited quinone proceeds from the triplet state (T_1) because intersystem crossing ($S_1 \rightarrow T_1$) in the excited state has high efficiency (0.8–1). Actually, the phosphorescence spectrum of 2-methyl-1,4-naphthoquinone was quenched in the presence of 1,1-diphenylethylene, for example ($k_q \tau \approx 1.1 \times 10^3$ M^{-1}, obtained directly from Stern–Volmer analysis, in ethanol at 77 K).

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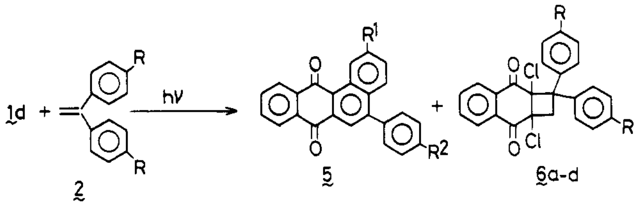
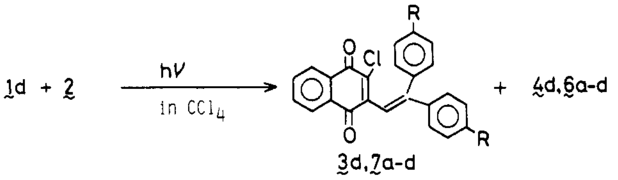
Table II. Photochemical Reaction of 2,3-Dichloro-1,4-naphthoquinone (1d) with *p*-Disubstituted 1,1-Diphenylethylene (2)



ethylene	irradiation time, h[b]	products (yield %)[a]	
		benz[*a*]anthracene-7,12-dione	cyclobutane adduct
2g, R = F	20	**5g**, $R^1 = R^2$ = F (27)	**6a**, R = F (56)
2h, R = Cl	20	**5h**, $R^1 = R^2$ = Cl (27)	**6b**, R = Cl (53)
2e, R = Me	30	**5e**, $R^1 = R^2$ = Me (41)	**6c**, R = Me (0)
2b, R = OMe	70	**5b**, $R^1 = R^2$ = OMe (61)	**6d**, R = OMe (0)

[a] Isolated yields based on **1d**. [b] Irradiation was carried out in a benzene solution (25 mL) of **1d** (0.5 mmol), **2** (1 mmol), and pyridine (1 mmol) and was continued until the initially formed ethylene adduct was completely consumed.

Table III. Initial Stage Photoreactivity of 2,3-Dichloro-1,4-naphthoquinone (1d) with *p*-Disubstituted 1,1-Diphenylethylene (2) in Carbon Tetrachloride



starting ethylene	products (chemical yield %)[a] [quantum yields][b]	
	ethylene adduct	cyclobutane adduct
2g	**7a**, R = F (17) [0.05]	**6a**, (71) [0.22]
2h	**7b**, R = Cl (11) [0.04]	**6b**, (15) [0.04]
2a	**3d**, R = H (41) [0.11]	**4d**, (0) [0][c]
2e	**7c**, R = Me[d]	**6c**, (0) [0]
2b	**7d**, R = OMe (100) [0.06]	**6d**, (0) [0]

[a] Chemical yields were based on consumed starting quinone **1d** after 1-min irradiation (>340 nm). [b] Quantum yields were measured by using ferrioxalate actinometer under 366-nm irradiation. [c] Within 1-min irradiation, no cyclobutane adduct could be detected. [d] Since the formation of **5e** was very fast, **5e** as well as ethylene adduct **7c** were formed even in the initial stage.

Table IV. Relationship between the Photoproducts and the Quinone Reduction Potentials[a]

quinone (1)	$E_{1/2}(1^{-}\cdot/1)$	ethylene adduct formation	ΔG, kcal/mol[b]
1c	-0.76_7	+	-7.1
1d	-0.77_2	+	-7.0
1b	-0.85_5	+	-5.0
1a	-0.92_3	+	-3.5
1e	-0.96_7	−	-2.5[c]
1f	-1.10_9	−	+0.8
1g	-1.15_0	−	+1.8

[a] Obtained by cyclic voltammetry: Pt electrode, tetraethylammonium perchlorate (TEAP, 0.1 M) in acetonitrile solution vs. Ag/0.01 M $AgNO_3$. [b] Calculated free energy change (ΔG) for photoinduced electron-transfer process from **2a** to photoexcited quinone (1*) and based on $\Delta E_{0,0}$, $E_{1/2}$ $(1^{-}\cdot/1)$, and $E_{1/2}(\mathbf{2a}/\mathbf{2a}^{+}\cdot)$. [c] See ref 15b.

the reaction solvent affects the amount of **3** formed.[9] Adduct **3** undergoes symmetry allowed[10] photochemical [π2s + π4a] cyclization followed by trans β-elimination of HX to be stabilized by aromatization (Scheme II). Similar [π2s + π4a] cycloaddition is known in the photochemical reactions of stilbene derivatives.[11] The results of the photochemical reactions of substituted 1,4-naphthoquinones **1a–g** with 1,1-diphenylethylene (**2a**) are summarized in Table I.

On the other hand, cyclobutane adduct **4g** was obtained by the photochemical reaction of **1g** with **2a**. Formation of **4** results from photochemical [π2s + π2s] cycloaddition, which is symmetry allowed. Cyclobutane formation is well-known in the photoreactions of substituted 1,4-naphthoquinones with many alkyl- and arylethylenes, e.g., styrene.[12] In the reactions of **1e**, **1f**, and **1g** with **2a**, only cyclobutane adducts **4e–g** were formed.

In the reactions of **1c** and **1d**, however, cyclobutane adducts **4c** and **4d** were formed in addition to the ethylene adducts. Cyclobutane adduct **4d** was so stable thermally and photochemically under the reaction conditions that it was not converted into the ethylene adduct **3d** or the benz[*a*]anthracene-7,12-dione **5a**. Thus the ethylene adduct **3** cannot be formed from **4** under our reaction conditions. The results of photochemical reactions of **1d** with several para-disubstituted 1,1-diphenylethylenes (**2b**, **2e**, **2g**, and **2h**) are shown in Table II. In the photoreactions of **1d** with **2g** and **2h**, cyclobutane adducts **6a** and **6b** were produced accompanied by benz[*a*]anthracene-7,12-diones **5g** and **5h**. However, in the reactions of **1d** with more electron-donating ethylenes such as **2e** and **2b**, no cyclobutane adducts were formed, and the only products were benz[*a*]anthracene-7,12-dione derivatives **5e** and **5b**.

Photoreactivities of **1d** with para-disubstituted 1,1-diphenylethylenes **2a**, **2b**, **2e**, **2g**, and **2h** at the initial stages in carbon tetrachloride[13] are summarized in Table III. Formation of the ethylene adducts and the cyclobutane adducts as well as consumption of **1d** were followed by HPLC. When **2g** was used as the starting ethylene, both cyclobutane adduct **6a** (71%) and ethylene adduct **7a** (17%) were formed. Although similar products **6b** and **7b** were afforded by the photoreaction of **1d** with **2h**, the yield of **6b** was lower (15%). On the contrary, when more electron-donating ethylenes such as **2a**, **2e**, and **2b** were subjected to the reaction, cyclobutane adducts **3d**, **6c**, and

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(9) The formation of **3g** by reaction of **1g** with **2a** was not affected by the polarity of solvents used (benzene, chloroform, methylene chloride, ethanol, methanol, and acetonitrile).

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(13) (a) Similar behavior of ethylene adduct formation was also observed in benzene. (b) Quantum yields of ethylene adduct formation are 0.04–0.11. The quantum yield of **7d** is lower than that of **3d**. This may result from the fact that the ion radical pair state between **1d** and **2b** ($\mathbf{1d}^{-}\cdot\mathbf{2b}^{+}\cdot$) is more stabilized than $\mathbf{1d}^{-}\cdot\mathbf{2a}^{+}\cdot$.

6d were not detected at the initial stages but the yields of ethylene adducts **4a** and **7d** increased. The most electron-donating ethylene (**2b**) gave a quantitative yield of ethylene adduct **7d**. Thus increase in the electron-donating character of the starting ethylene (**2b** > **2e** > **2a** > **2h** > **2g**) favors ethylene adduct formation.

Whether the ethylene adduct **3** or the cyclobutane adduct **4** is formed in the photoreaction of **1** with **2** depends not only upon the electron-donating ability of ethylene **2** but also upon the electron-accepting ability of quinone **1**. The reduction potentials of substituted 1,4-naphthoquinones **1a**–**g** were measured by cyclic voltammetry. Quinones **1a**–**d**, with higher reduction potentials, form ethylene adducts in the reactions with 1,1-diphenylethylene **2a** (Table IV).

The free energy change (ΔG) in the photoinduced electron-transfer process between quinone **1** and 1,1-diphenylethylene (**2a**) is given by[14]

$$\Delta G = 23.06[E_{1/2}(\mathbf{2a}/\mathbf{2a}^{+}\cdot) - E_{1/2}(\mathbf{1}^{-}\cdot/\mathbf{1}) - e_0^2/a\epsilon] - \Delta E_{0,0}\ (\text{kcal/mol}) \quad (1)$$

where $E_{1/2}(\mathbf{2a}/\mathbf{2a}^{+}\cdot)$ is the oxidation potential of **2a**, and $E_{1/2}(\mathbf{1}^{-}\cdot/\mathbf{1})$ is the reduction potential of **1**. The Coulombic attraction term $e_0^2/a\epsilon$ is the energy gained by bringing the two ion radicals to the encounter distance "a" in a solvent of dielectric constant ϵ, and $\Delta E_{0,0}$ is the electronic excitation energy of **1**. For 1,1-diphenylethylene $E_{1/2}(\mathbf{2a}/\mathbf{2a}^{+}\cdot)$ is estimated to be +1.42 V vs. Ag/0.01 M Ag^{+}.[15] We assume that the Coulombic attraction term ($e_0^2/a\epsilon$) is too small to influence the present reactions. The lowest excitation energies of **1a**–**g** are evaluated to be ca. 57.5 kcal/mol.[16] Equation 1 allows us to estimate ΔG for photoinduced electron transfer from **2a** to **1** (Table IV). In the photochemical reactions in which the calculated ΔG values were smaller than −3.0,[17] we actually obtained the ethylene adducts.

These results indicate that the formation of the ethylene adduct proceeds via initial photoinduced electron transfer from ethylene **2** to quinone **1**.

In addition, direct evidence for the electron-transfer process was obtained by the CIDNP technique.[18] When a methanol-d_4 solution of **1d** and **2b** was irradiated (>370 nm) under argon,[19] strong ^{1}H CIDNP signals were observed, which were attributable to the methylene H, the aromatic ring H, and the methoxy H of **2b**;[20] the methylene H and the ring H (ajacent to methoxy group) showed enhanced absorption, whereas the methoxy H and the ring H (ajacent to ethylene moiety) showed enhanced emission. Upon irradiation of **1d** in the presence of **2b** in acetonitrile-d_3, CIDNP signals were also detected. CIDNP signals were also observed when **1d** was irradiated in the presence of **2c**, **2d**, or **2e** in acetonitrile-d_3 or methanol-d_4.[19]

These CIDNP signals clearly indicate that the photoinduced electron transfer from **2** to **1d** generates an ion radical pair, which in turn regenerates **1d** and **2** via back electron transfer. By analyzing the polarization pattern on the basis of Kaptein's rule,[21] the ion radical pair is suggested to have the triplet multiplicity $(\overline{\mathbf{1d}^{-}\cdot\mathbf{2}^{+}\cdot})^3$.[22] Similarly, the formation of other ethylene adducts (Table I) can be understood by taking into consideration the contribution of the triplet ion radical pair.

A mixture of **1d** and **2b** was irradiated (>340 nm) in several solvents. The amount of **7d** produced was followed by HPLC. Ethylene adduct formation in carbon tetrachloride[13a] was about eight times faster than that in methylene chloride.[9] On the contrary, the ethylene adduct formation was not detected on irradiating in ethanol or methanol within 2 min, although prolonged irradiation did give **7d**. Thus use of a highly polar solvent represses ethylene adduct formation.

CIDNP signals could not be detected in nonpolar solvents such as benzene-d_6, carbon tetrachloride, and chloroform-d. Observation of CIDNP signals requires a suitable distance (ca. 9 Å) between anion radical and cation radical and a certain lifetime in the ion radical pair.[25] In nonpolar solvents, the distance between the two radical species may be smaller because of the weak solvation and the lifetime of the ion radical pair may be shorter (>10 times) than those in polar solvents. The coupling of the two ion radicals requires close encounter with each other. In a nonpolar solvent, the quinone anion radical and the ethylene cation radical may exist closely enough to couple in a solvent cage. In a polar solvent, the solvated ion radicals could be drawn apart (ca. 9 Å) to the extent that ethylene adduct formation would be unfavorable. Nevertheless, we believe that even in a polar solvent the ion radical pair $\overline{\mathbf{1}^{-}\cdot\mathbf{2}^{+}\cdot}^{3}$ is not sufficiently dissociated to form solvated ion radicals under our conditions at room temperature.[26]

Since a broad electronic absorption (maximum at ~410 nm, absorbance ~0.02) attributable to a charge-transfer (CT) complex was observed in a benzene solution of **1d** (2 mM) and a large amount of **2b** (75 mM),[27] the possibility of electron transfer from the photoexcited CT complex could not be excluded. However, the actual photoreaction proceeded even in a very dilute solution in which the CT spectrum could not be detected. Consequently, the ion radical pair may not result from the photoexcited CT complex, but from direct electron transfer from ethylene

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[14] Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

[15] The estimated value (see ref 8a) for $E_{1/2}$ $(\mathbf{2a}/\mathbf{2a}^{+}\cdot)$ is +1.48 eV vs. Ag/0.1 M Ag^{+}; see the Experimental Section.

[16] Kuboyama, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2771.

[17] (a) The relationship between the photoreaction products **3** and/or **4** and the calculated ΔG values is not linear because of some deviation of the actual ΔG from the calculated ΔG value due to participation of the Coulombic attraction term ($e_0^2/a\epsilon$) and of the actual excitation energy ($\Delta E_{0,0}$) for each 1,4-naphthoquinone. (b) Although the calculated ΔG for **1e** had a small negative value, the ethylene adduct **4e** was not formed. In this case, the actual ΔG value for **1e** may be positive, probably because of small errors in estimating the actual excitation energy and the actual Coulombic attraction term.

[18] Maruyama, K.; Tai, S.; Otsuki, T. *Chem. Lett.* **1983**, 843.

[19] During the CIDNP measurement, a detectable consumption of **1d** and production of the ethylene adduct were not observed. However, prolonged irradiation gave the ethylene adduct and benz[*a*]anthracene-7,12-dione derivatives.

[20] Upon irradiation, ^{1}H NMR signals of the ring protons of **1d** showed broadening.

[21] Kaptein, R. *J. Chem. Soc., Chem. Commun.* 1971, 732.

[22] The *g* value of the 1,1-diarylethylene cation radical is assumed to be smaller than that of the quinone anion radical.[23] The sign of hfcc of 1,1-diarylethylene (**2**) was estimated on the basis of its Hückel molecular orbital calculation.[24]

[23] Fischer, H.; Hellwege, K.-H. "Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, Vol. 9, Magnetic Properties of Free Radicals"; Springer-Verlag: Berlin-Heidelberg-New York, 1980.

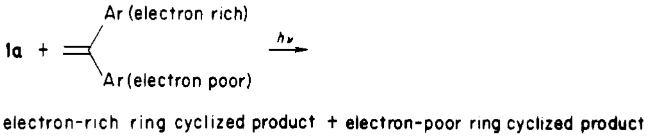
[24] Heilbronner, E.; Bock, H. "The HMO Model and its Application, 3, Tables of Hückel Molecular Orbitals"; English translation by Martin, W., Rackstraw, A. J.; John Wiley & Sons: London/New York/Sydney/Toronto, 1976; pp 117.

[25] Turro, N. J. "Modern Molecular Photochemistry"; The Benjamin/Cummings Publishing Co., Inc.: Menlo Park, CA, 1978; pp 278.

[26] In a polar solvent (CH_3CN), easy dissociation of ion radical pair was reported in a photo-induced electron-transfer reaction between cyanated aromatics and 1,1-diphenylethylene.[8] In this case, the dissociated 1,1-diphenylethylene cation radical was trapped as a methanol or cyanide adduct,[8a,b] and the dissociated anion radical of a cyanated aromatic compound was detected by ESR.[8c] In our system, a similar adduct could not be detected in the presence of methanol. Furthermore, the CIDNP results indicate that ion radical pair $\overline{\mathbf{1}^{-}\cdot\mathbf{2}^{+}\cdot}^{3}$ is formed even in polar solvents (CD_3OD and CD_3CN).

[27] The weak CT complex could not be excited directly because the weak CT spectrum overlapped that of **1d**.

Table V. Photochemical Reaction of 2-Bromo-3-methoxy-1,4-naphthoquinone (1a) with Unsymmetrical 1,1-Diarylethylene



1,1-diarylethylene		product yields, %[a]	
Ar (electron rich)	Ar (electron poor)	electron-rich ring cyclized product	electron-poor ring cyclized product
2-furyl	phenyl	31	0
2-thienyl	phenyl	62	8
2-*N*-methylpyrrolyl	phenyl	50	0
2-benzo[*b*]thienyl	phenyl	32	17
2-*N*-methylindolyl	phenyl	61	0
phenyl	3-pyridyl	60	0
phenyl	4-pyridyl	15	0

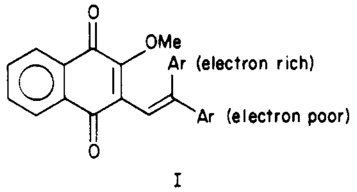
[a] Isolated yields based on **1a**.

2 to photoexcited quinone (**1***).

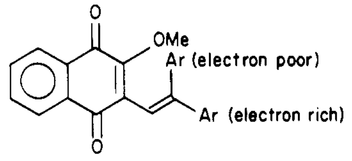
If halide anions could be readily released from the quinone anion radical, the coupling reaction between quinone anion radical and ethylene cation radical should occur after elimination of a halide anion from the quinone anion radical (Scheme II). However, the results of many investigations of the anion radicals of 2- and 2,3-halogenated 1,4-naphthoquinones[7a–d] indicate that elimination of halide anion from the quinone anion radical is difficult. Therefore it is probable that halide anion is released with a proton as hydrogen halide from the intermediate after coupling of quinone anion radical with ethylene cation radical.

In conclusion, formation of the ethylene adduct proceeds via (i) photoinduced electron transfer from 1,1-diarylethylene to photoexcited quinone affording ion radical pair $\mathbf{1}^{-}\cdot\mathbf{2}^{+}\cdot$[3] and (ii) coupling of the ion radicals in a solvent cage followed by elimination of hydrogen halide.

Upon prolonged irradiation, the ethylene adduct **3** is transformed into a benz[*a*]anthracene-7,12-dione derivative **5** via photochemical [$\pi 2s + \pi 4a$] cyclization[10] followed by trans β-elimination of HX (for X = OMe, Cl, Br) or oxidation (for X = H), becoming stabilized by aromatization. Similar aromatic cyclizations have been observed in the photocyclization of stilbene analogues.[11,28] The stilbene analogues 2-, 3-, and 4-styrylpyridines[28] as well as 2-styrylthiophene, 3-styrylbenzothiophene, and 2-styrylfuran[28] all undergo photocyclization into the corresponding aromatics from cis conformations, although in some stilbene-like compounds the trans isomers are energetically more favorable than the cis isomers.[29] As reported previously,[30] in the photochemical reactions of **1a** with unsymmetrical 1,1-diarylethylenes containing heterocyclic aromatic rings, the more electron-rich aromatic ring predominantly cyclizes to give a polycyclic system (Table V). Of the two possible isomers of the ethylene adduct, formation of isomer I would be preferred over isomer II because of the stronger intramolecular charge-transfer attraction between the quinone moiety and the electron-rich aromatic ring.



I



II

The ensuing trans β-elimination of HX (for X = OMe) should proceed by an ionic pathway. For example, upon irradiation of a benzene solution of **3a**, we identified methanol but no formaldehyde by gas chromatography. Consequently, the final cyclization step to a benz[*a*]anthracene-7,12-dione should proceed via concerted or synchronous photochemical [$\pi 2s + \pi 4a$] cyclization followed by trans β-elimination of HX in an ionic manner. Accordingly, the reaction follows the path indicated by the starred arrows in Scheme II.

Reactions of **1a** with **2a–f** are summarized in Table VI. Quinone **1a** reacts with many 1,1-diarylethylenes to produce polycyclic aromatic quinones.[4,30] However, styrene and 1,1-bis[(*p*-(dimethylamino)phenyl]ethylene do not give corresponding products in photoreactions with **1a–d**,[31] although they undergo Diels–Alder reactions with 1,4-naphthoquinone[3,32] to afford benz[*a*]anthracene-7,12-dione derivatives.

A variety of quinones with the 2-bromo-3-methoxy-1,4-quinone skeleton undergo the reaction. When a mixture of 6-bromo-7-methoxy-5,8-quinoxalinedione (**8**) and **2a** was irradiated we isolated a product **9a**, whose IR and NMR spectra, mass spectrum, and elemental analysis indicated the structure 5-phenylnaphtho[1,2-*g*]quinoxaline-7,12-dione. Similar photochemical reactions of **8** with other 1,1-diarylethylenes **2b–f** afforded the new naphtho[1,2-*g*]quinoxaline-7,12-dione derivatives **9b–f** (Table VII).

Similar reaction of 2-bromo-3-methoxy-1,4-quinones gave several novel polycyclic aromatic quinones. Dibenz[*a,j*]anthracene-7,14-diones (**11**),[33] naphtho[2,1-*b*]chrysene-7,14-diones (**13**),[33] naphtho[2,1-*g*]quinoline-7,12-diones (**15**),[34] and naphtho[1,2-*g*]quinoline-7,12-diones (**17**)[35] were synthesized by photoreactions of the corresponding quinones **10**, **12**, **14**, and **16** with **2a–f**, respectively (Scheme III).

Related syntheses were carried out by photoreactions of halogenated 1,4-naphthoquinones with alkoxyethylenes. Upon irradiation of 2,3-dichloro-1,4-naphthoquinone (**1d**) in the presence of alkyl vinyl ethers **18a–c** or vinyl acetates **19a,b**, we observed formation of ethylene adduct **20** or cyclobutane adduct **21** (Scheme IV).[36] As in the reactions

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(28) Blackburn, E. V.; Timmons, C. J. *Q. Rev., Chem. Soc.* **1967**, *23*, 482.

(29) (a) Arai, T.; Karatsu, T.; Sakuragi, H.; Tokumaru, K. *Chem. Lett.* **1981**, 1377. (b) Arai, T.; Sakuragi, H.; Tokumaru, K.; Sakaguchi, Y.; Nakamura, J.; Hayashi, H. *Chem. Phys. Lett.* **1983**, *98*, 40. (c) Arai, T.; Karatsu, T.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1983**, *24*, 2873.

(30) Maruyama, K.; Otsuki, T.; Mitsui, K.; Tojo, T. *J. Heterocycl. Chem.* **1980**, *17*, 695.

(31) Styrene has a higher oxidation potential than **2a**. The ΔG value for photo-induced electron transfer is positive, so that the present reaction is not possible. In the reaction with 1,1-bis(*p*-(dimethylamino)-phenyl)ethylene, a facile photo-induced electron transfer from the dimethylamino moiety to the quinone could occur rather than from the ethylene moiety, so that the present reaction products could not be obtained.

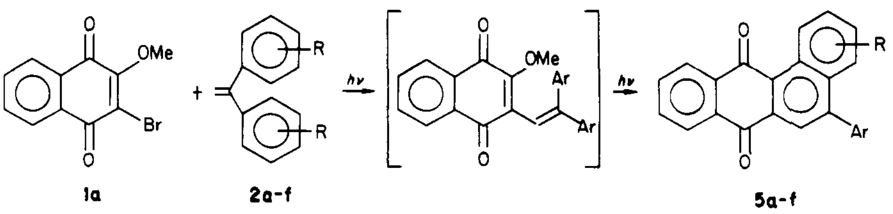
(32) Gates, M. *J. Org. Chem.* **1982**, *47*, 578.

(33) Maruyama, K.; Otsuki, T.; Tai, S. *Nippon Kagaku Kaishi* **1984**, 90.

(34) Maruyama, K.; Tai, S.; Otsuki, T. *Heterocycles* **1983**, *20*, 1031.

(35) Maruyama, K.; Tai, S.; Otsuki, T. *Chem. Lett.* **1981**, 1565.

Table VI. Photochemical Reactions of 2-Bromo-3-methoxy-1,4-naphthoquinone (1a) with 1,1-Diarylethylenes (2a–f)



starting ethylene	irradiation time, h[a]	product (yield %)[b]
2a, R = H	3.5	**5a**, R = H; Ar = Ph (49)
2b, R = *p*-OMe	21	**5b**, R = 2-OMe; Ar = *p*-OMeC$_6$H$_4$ (65)
2c, R = *m*-OMe	8	**5c**, R = 3-OMe; Ar = *m*-OMeC$_6$H$_4$ (32)
2d, R = *o*-OMe	6	**5d**, R = 4-OMe; Ar = *o*-OMeC$_6$H$_4$ (25)
2e, R = *p*-Me	5	**5e**, R = 2-Me; Ar = *p*-MeC$_6$H$_4$ (65)
2f, R = *m*-Me	3.5	**5f**, R = 3-Me; Ar = *m*-MeC$_6$H$_4$ (48)

[a] Irradiation was carried out in a benzene solution (25 mL) of **1a** (0.5 mmol), **2** (1 mmol), and pyridine (1 mmol) and was continued until the initially formed ethylene adduct was completely consumed. [b] Isolated yield based on **1a**.

Scheme III. Regioselective Syntheses of Polycyclic Aromatic Quinones (11, 13, 15, and 17)

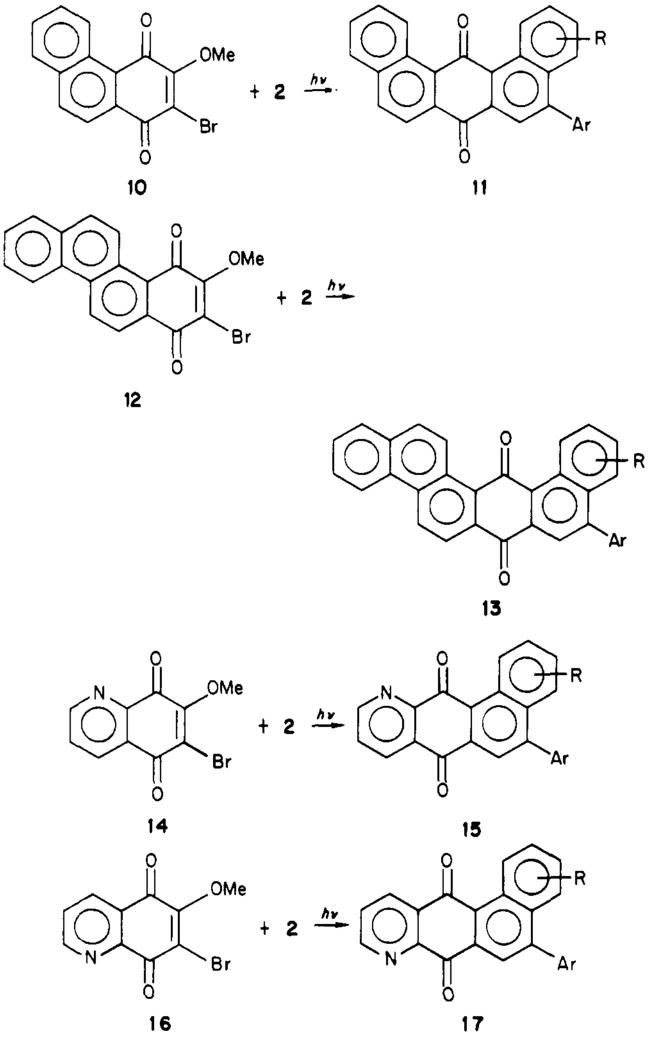
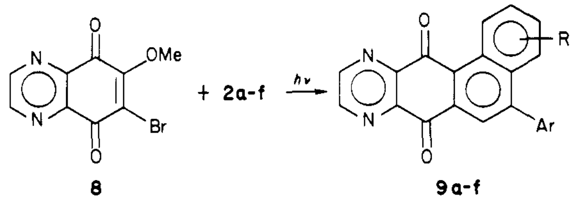


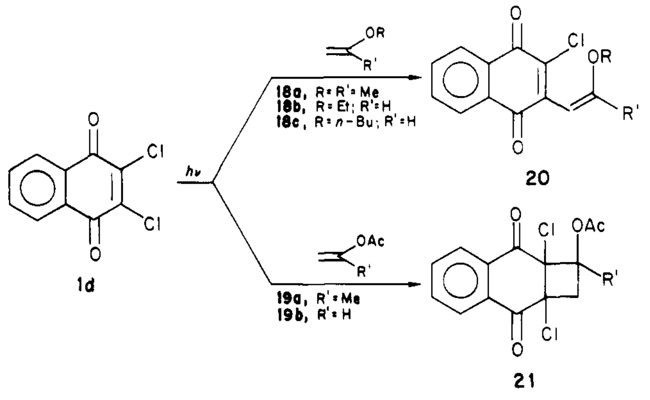
Table VII. Photochemical Syntheses of Naphtho[1,2-*g*]quinoxaline-7,12-dione Derivatives (9a–f)



starting ethylene	irradiation time, h[a]	product (yield %)[b]
2a	2	**9a**, R = H; Ar = Ph (12)
2b	23	**9b**, R = 2-OMe; Ar = *p*-OMeC$_6$H$_4$ (6)
2c	1.3	**9c**, R = 3-OMe; Ar = *m*-OMeC$_6$H$_4$ (23)
2d	3	**9d**, R = 4-OMe; Ar = o-OMeC$_6$H$_4$ (4)
2e	7.5	**9e**, R = 2-Me; Ar = *p*-MeC$_6$H$_4$ (9)
2f	3.5	**9f**, R = 3-Me; Ar = *m*-MeC$_6$H$_4$ (12)

[a] Irradiation was carried out in a benzene solution (400 mL) of **8** (1 mmol), **2** (2 mmol), and pyridine (1 mmol) and was continued until the initially formed ethylene adduct was completely consumed. [b] Isolated yield based on **8**.

Scheme IV. Photochemical Reactivities of 1d with Alkyl Vinyl Ethers (18a–c) or Vinyl Acetates (19a,b)



of **1d** with 1,1-diarylethylenes, whether **20** or **21** was formed as the major product depended upon the electron-donating character of the starting ethylenes **18** and **19**. The ethylene adduct **20** was formed exclusively in the reactions with alkyl vinyl ethers, which are more electron donating than vinyl acetates. Similarly, isopropenyl methyl ether (**18a**) reacted with **1a** and **1c** to give the corresponding ethylene adducts. These adducts were unstable under acidic conditions and formed β-keto alkylated 1,4-naphthoquinone after hydrolysis. This method can be used for synthesis of a wide variety of β-keto alkylated 1,4-naphthoquinones.

Experimental Section

All melting points were determined with a Yanagimoto micro melting point apparatus and uncorrected. Mass spectra were taken on a Hitachi M-52 mass spectrometer or a JEOL JMS-DX300 mass spectrometer. The electronic spectra were obtained by using a Shimadzu UV-200 spectrometer. ^{1}H NMR spectra were

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(36) See details in the following report: Maruyama, K.; Otsuki, T.; Tai, S. *Chem. Lett.* **1984**, 371.

taken by using a JEOL PS-100 spectrometer and chemical shifts were recorded in parts per million (ppm) on the δ scale from tetramethylsilane as an internal standard, while the IR spectra were obtained by using a JASCO IRA-1 spectrometer on KBr pellets. High-pressure liquid chromatography was carried out by using Japan Waters Model 440 absorbance detector equipped with Altex pump Model 110A and Japan Waters microporasil analytical column; 3.9 × 300 mm. Elemental analyses were performed at the microanalytical laboratory of Kyoto University.

Starting Materials. All 1,1-diarylethylenes (**2a–h**), 2,3-dichloro-1,4-naphthoquinone (**1d**), and 2-methyl-1,4-naphthoquinone (**1f**) were commercially available from Nakarai Chemicals Co., Ltd., Tokyo Chemical Industry Co., Ltd., and Wakenyaku Co., Ltd. 2-Methoxy- (**1g**),[37] 2-bromo-3-methoxy- (**1a**),[38] 2,3-dibromo- (**1c**),[39] 2-bromo- (**1b**),[40] and 2-bromo-3-methyl-1,4-naphthoquinone (**1e**)[41] were synthesized according to methods described in the literature.

Preparation of 6-Bromo-7-methoxy-5,8-quinoxalinedione (8). To a solution of 6-methoxy-5,8-quinoxalinedione[42] (0.61 g, 3.21 mmol) and sodium acetate (2.15 g) in acetic acid (19 mL) was added bromine (0.18 mL). The solution was stirred overnight. After addition of water (250 mL), the solution was extracted with chloroform. The organic layer was washed once with saturated $NaHCO_3$ solution and twice with saturated NaCl solution. Evaporation of the solvent and recrystallization of the residue from ethanol gave **8** as yellow needles: yield 58%: ^1H NMR ($CDCl_3$) δ 8.98 (2 H, s), 4.40 (3 H, s); mp 174 °C dec; IR (KBr) 1685 cm^{-1}; UV ($CHCl_3$) λ_{max} 279 nm (log ϵ 4.29), 385 (3.32); mass spectrum, *m/e* 267 (M^+), 269 (M^+). Anal. Calcd for $C_9H_5O_3N_2Br$: C, 40.18; H, 1.87; N, 10.41; Br, 29.70. Found: C, 40.60; H, 1.78; N, 10.41; Br, 29.74.

General Procedure for the Preparative Photochemical Reaction. A solution of **1** (1 mmol) and **2** (2 mmol) in benzene (25 mL) was irradiated at room temperature with a high-pressure Hg lamp (300 W) in the presence of pyridine (2 mmol). The amount of **1** consumed and products formed were followed by TLC. Irradiation was continued for the times shown in Table I. For the reactions of **1a–d**, irradiation time was based upon disappearance of the intermediate ethylene adduct (**3**), whereas those of **1e–g** were based upon disappearance of the starting quinone. After irradiation, the reaction mixture was concentrated in vacuo and separated by column chromatography on silica gel and by fractional recrystallization to give **5** and/or **4**. If, in the reactions of **1a–d**, irradiation was stopped after complete consumption of the starting quinone, **3** was also obtained as a product.

Physical Properties of Benz[*a*]anthracene-7,12-dione Derivatives.[43] **3-Methoxy-5-(*m*-methoxyphenyl)benz[*a*]anthracene-7,12-dione (5c)**: yellow needles (from hexane–chloroform); mp 191–192 °C; ^1H NMR ($CDCl_3$) δ 9.72 (1 H, d, *J* = 10 Hz), 8.28 (1 H, s), 8.1–8.4 (2 H, m), 7.6–7.9 (2 H, m), 6.9–7.5 (6 H, m), 3.87 (3 H, s), 3.79 (3 H, s); IR (KBr) 1660, 1610, 1470, 1295, 1240 cm^{-1}; UV ($CHCl_3$) λ_{max} 252 nm (log ϵ 4.35), 311 (4.51), 392 (3.68). Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.89; H, 4.35.

4-Methoxy-5-(*o*-methoxyphenyl)benz[*a*]anthracene-7,12-dione (5d): orange needles (from hexane–chloroform); mp 176–177 °C; ^1H NMR ($CDCl_3$) δ 9.42 (1 H, d, *J* = 9 Hz), 8.1–8.4 (2 H, m), 8.17 (1 H, s), 6.8–7.9 (8 H, m), 3.66 (3 H, s), 3.49 (3 H, s); IR (KBr) 1670, 1580, 1460, 1290, 1280, 1250 cm^{-1}; UV ($CHCl_3$) λ_{max} 251 nm (log ϵ 4.39), 282 (4.20), 312 (4.37), 466 (3.41). Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.96; H, 4.54.

2-Methyl-5-(*p*-tolyl)benz[*a*]anthracene-7,12-dione (5e): yellow needles (from hexane–chloroform); mp 244.5–245.5 °C; ^1H NMR ($CDCl_3$) δ 9.60 (1 H, br-s), 8.23 (1 H, s), 8.1–8.4 (2 H, m), 7.7–8.0 (3 H, m), 7.2–7.5 (5 H, m), 2.61 (3 H, s), 2.47 (3 H, s); IR (KBr) 1660, 1290, 720 cm^{-1}; UV ($CHCl_3$) λ_{max} 256 nm (log ϵ 4.52), 295 (4.55), 373 (3.54), 429 (3.68). Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.17; H, 5.01. Found: C, 86.12; H, 4.92.

2-Fluoro-5-(*p*-fluorophenyl)benz[*a*]anthracene-7,12-dione (5g): lemon yellow needles (from hexane–chloroform); mp 242–243 °C; ^1H NMR ($CDCl_3$) δ 9.77 (1 H, dd, *J* = 12.5, 2.5 Hz), 8.1–8.5 (2 H, m), 8.30 (1 H, s), 7.1–8.1 (8 H, m); IR (KBr) 1655, 1570, 1420, 1280, 710 cm^{-1}; UV ($CHCl_3$) λ_{max} 252 nm (log ϵ 4.43), 257 (4.42) sh, 288 (4.56), 420 (3.68). Anal. Calcd for $C_{24}H_{12}O_2F_2$: C, 77.83, H, 3.27; F, 10.26. Found: C, 77.85; H, 3.14; F, 10.15.

2-Chloro-5-(*p*-chlorophenyl)benz[*a*]anthracene-7,12-dione (5h): lemon yellow needles (from hexane–chloroform); mp 260–261 °C; ^1H NMR ($CDCl_3$) δ 9.96 (1 H, d, *J* = 2 Hz), 8.2–8.5 (2 H, m), 8.32 (1 H, s), 7.2–8.0 (8 H, m); IR (KBr) 1665, 1580, 1285, 715 cm^{-1}; UV ($CHCl_3$) λ_{max} 253 nm (log ϵ 4.50), 291 (4.55), 419 (3.66). Anal. Calcd for $C_{24}H_{12}O_2Cl_2$: C, 71.48; H, 3.00. Found: C, 71.09; H, 2.80.

Physical Properties of the Ethylene Adducts.[43] **2-(2,2-Diphenylethenyl)-1,4-naphthoquinone (3b)**: orange crystals (from hexane–chloroform): mp 150–152 °C; ^1H NMR ($CDCl_3$) δ 7.7–8.0 (2 H, m), 7.4–7.6 (2 H, m), 7.0–7.3 (11 H, m), 6.15 (1 H, d, *J* = 1 Hz); IR (KBr) 1650, 1560, 1335, 1300 cm^{-1}; high-resolution mass spectrum calcd for $C_{24}H_{16}O_2$ 336.1155, found 336.1144.

2-Bromo-3-(2,2-diphenylethenyl)-1,4-naphthoquinone (3c): yellow needles (from hexane–chloroform); mp 192.5–193.5 °C; ^1H NMR ($CDCl_3$) δ 8.14 (1 H, m), 7.5–7.8 (3 H, m), 7.42 (5 H, s), 7.21 (5 H, s), 6.68 (1 H, s); IR (KBr) 1660, 1270, 680, 675 cm^{-1}; high-resolution mass spectrum calcd for $C_{24}H_{15}O_2$ ^{81}Br 416.0236 and $C_{24}H_{15}O_2$ ^{79}Br 414.0237, found 416.0179 and 414.0151.

2-Chloro-3-(2,2-diphenylethenyl)-1,4-naphthoquinone (3d): yellow needles (from hexane–chloroform): mp 200–201 °C; ^1H NMR ($CDCl_3$) δ 8.09 (1 H, m), 7.5–7.9 (3 H, m), 7.38 (5 H, s), 7.19 (5 H, s), 6.73 (1 H, s); IR (KBr) 1665, 1280 cm^{-1}; high-resolution mass spectrum calcd for $C_{24}H_{15}O_2{}^{35}Cl$ 370.0760, found 370.0685.

2-Chloro-3-[2,2-bis(*p*-fluorophenyl)ethenyl]-1,4-naphthoquinone (7a): yellow needles (from hexane–chloroform); mp 212–213 °C; ^1H NMR ($CDCl_3$) δ 8.1–8.3 (1 H, m), 7.7–8.0 (3 H, m), 6.8–7.5 (8 H, m), 6.69 (1 H, s); IR (KBr) 1665, 1510, 1280 cm^{-1}; high-resolution mass spectrum calcd for $C_{24}H_{13}O_2{}^{35}ClF_2$ 406.0572, found 406.0584.

2-Chloro-3-[2,2-bis(*p*-chlorophenyl)ethenyl]-1,4-naphthoquinone (7b): yellowish orange needles (from hexane–chloroform); mp 205–206 °C; ^1H NMR ($CDCl_3$) δ 8.1–8.3 (1 H, m), 7.6–8.0 (3 H, m), 7.36 (4 H, s), 7.25 (2 H, d, *J* = 9 Hz), 7.10 (2 H, d, *J* = 9 Hz), 6.71 (1 H, s); IR (KBr) 1665, 1285, 835 cm^{-1}; high-resolution mass spectrum calcd for $C_{24}H_{13}O_2{}^{35}Cl_3$ 437.9981, found 438.0007.

2-Chloro-3-[2,2-bis(*p*-tolyl)ethenyl]-1,4-naphthoquinone (7c): yellow flakes (from hexane–chloroform); mp 175–177 °C; ^1H NMR ($CDCl_3$) δ 8.0–8.2 (1 H, m), 7.6–7.9 (3 H, m), 7.29 (2 H, d, *J* = 8.5 Hz), 7.16 (2 H, d, *J* = 8.5 Hz), 7.02 (4 H, s), 6.65 (1 H, s), 2.40 (3 H, s), 2.28 (3 H, s). IR (KBr) 1665, 1280, 1245 cm^{-1}; high-resolution mass spectrum calcd for $C_{26}H_{19}O_2{}^{35}Cl$ 398.1074, found 398.1097.

2-Chloro-3-[2,2-bis(*p*-methoxyphenyl)ethenyl]-1,4-naphthoquinone (7d): reddish orange needles (from hexane–chloroform); mp 141–142.5 °C; ^1H NMR ($CDCl_3$) δ 7.8–8.0 (1 H, m), 7.6–7.8 (1 H, m), 7.39 (2 H, d, *J* = 9 Hz), 7.17 (2 H, d, *J* = 9 Hz), 6.97 (2 H, m), 6.80 (2 H, d, *J* = 9 Hz), 6.65; (1 H, s), 6.58 (2 H, d, *J* = 9 Hz), 3.36 (3 H, s), 3.19 (3 H, s); IR (KBr) 1670, 1510, 1285, 1245 cm^{-1}; high-resolution mass spectrum calcd for $C_{26}H_{19}O_4{}^{35}Cl$ 430.0971, found 430.0961.

Physical Properties of the Cyclobutane Adducts.[44] **1,6-Dichloro-8,8-diphenyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione (4d)**: colorless crystals (from hexane–chloroform); mp 171–172 °C dec; ^1H NMR ($CDCl_3$) δ 8.24 (1 H, m), 8.00 (1 H, m), 7.74 (2 H, m), 7.2–7.6 (7 H, m), 6.8–7.1 (3 H, m), 4.41 (1 H, d, *J* = 12.5 Hz), 3.59 (1 H, d, *J* = 12.5 Hz); IR (KBr) 1685, 1585, 1260, 695 cm^{-1}. Anal. Calcd for $C_{24}H_{16}O_2Cl_2$: C, 70.78; H, 3.96; Cl, 17.41. Found: C, 70.99; H, 3.79; Cl, 17.31.

6-Bromo-8,8-diphenyl-1-methyl-3,4-benzobicyclo[4.2.0]oct-3-ene-2,5-dione (4e): colorless crystals (from hexane–chloroform); mp 157–159 °C; ^1H NMR ($CDCl_3$) δ 8.10 (1 H, m), 7.82 (1 H, m), 7.1–7.7 (10 H, m), 6.7–7.0 (2 H, m), 4.03 (1 H, d, *J* = 12 Hz), 3.07 (1 H, d, *J* = 12 Hz), 1.56 (3 H, s); IR (KBr) 1680,

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[43] The physical properties of **5a,b,f** and **3a** are given in ref 4c.

[44] The physical properties of the other cyclobutane adducts (**4f,4f′,4g**) are given in ref 12a and 12b.

1260, 1245, 730, 695, 685 cm^{-1}. Anal. Calcd for $C_{25}H_{19}O_2Br$: C, 69.62; H, 4.44; Br, 18.53. Found: C, 69.89; H, 4.41; Br, 18.44.

1-Bromo-8,8-diphenyl-6-methyl-3,4-benzobicyclo[4.2.0]-oct-3-ene-2,5-dione (4e′): colorless flakes (from hexane–chloroform); mp 110–114 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.11 (2 H, m), 7.1–7.9 (10 H, m), 6.8–7.0 (2 H, m), 4.41 (1 H, d, J = 12 Hz), 3.45 (1 H, d, J = 12 Hz), 1.74 (3 H, s); IR (KBr) 1685, 1670, 1270, 740, 695 cm^{-1}. Anal. Calcd for $C_{25}H_{19}O_2Br$: C, 69.62; H, 4.44; Br, 18.53. Found: C, 69.78; H, 4.32; Br, 18.40.

1,6-Dichloro-8,8-bis(*p*-fluorophenyl)-3,4-benzobicyclo-[4.2.0]oct-3-ene-2,5-dione (6a): colorless needles (from hexane–chloroform); mp 167.5–168.5 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.1–8.3 (1 H, m), 7.9–8.1 (1 H, m), 7.7–7.9 (2 H, m), 7.2–7.6 (4 H, m), 7.11 (2 H, t, J = 9 Hz), 6.71 (2 H, t, J = 9 Hz), 4.39 (1 H, d, J = 12.5 Hz), 3.53 (1 H, d, J = 12.5 Hz); IR (KBr) 1685, 1585, 1505, 1265 cm^{-1}. Anal. Calcd for $C_{24}H_{14}O_2Cl_2F_2$: C, 65.03; H, 3.18; Cl, 16.00; F, 8.57. Found: C, 65.56; H, 3.16; Cl, 16.03; F, 8.52.

1,6-Dichloro-8,8-bis(*p*-chlorophenyl)-3,4-benzobicyclo-[4.2.0]oct-3-ene-2,5-dione (6b): colorless crystals (from hexane–chloroform); mp 195–196 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.1–8.3 (1 H, m), 7.9–8.1 (1 H, m), 7.7–7.9 (2 H, m), 7.40 (4 H, s), 7.23 (2 H, d, J = 9 Hz), 6.99 (2 H, d, J = 9 Hz), 4.38 (1 H, d, J = 12 Hz), 3.52 (1 H, d, J = 12 Hz); IR (KBr) 1690, 1585, 1490, 1255 cm^{-1}. Anal. Calcd for $C_{24}H_{14}O_2Cl_4$: C, 60.54; H, 2.96; Cl, 29.78. Found: C, 60.56; H, 2.84; Cl, 29.78.

Examination of the Initial Stage of the Photoreaction. Irradiation (>340 nm, through a Toshiba UV-36 glass filter) of a solution of 2,3-dichloro-1,4-naphthoquinone (4 mM), 1,1-diarylethylene (7 mM), and pyridine (10 mM) with a high-pressure Hg lamp in an appropriate solvent was done in a merry-go-round for several minutes. The amounts of starting materials, cyclobutane adduct, and ethylene adduct were determined by HPLC with a μ-porasil analytical column and 1–20% ether–hexane as eluents. Total conversion did not exceed 10%. Quantum yields were measured by using a ferrioxalate actinometer under 366-nm irradiation.

Reduction Potential Measurements. The reduction potentials of quinones were obtained by cyclic voltammetry. The working electrode was platinum wire. A Ag/Ag$^+$ (0.01 M) electrode was used as a reference electrode and 0.1 M tetraethylammonium perchlorate as supporting electrolyte.

The standard redox potential (E) in the system ($Ag^+ + e \rightleftarrows Ag\downarrow$) is given by[45]

$$E = 0.80 + 0.06 \log [Ag^+] \text{ (V)} \qquad (2)$$

where [Ag$^+$] is the concentration of Ag$^+$. For the system of Ag/0.1 M Ag$^+$, E = 0.74 V, whereas for Ag/0.01 M Ag$^+$, E = 0.68 V. Consequently, the oxidation potential of 1,1-diphenylethylene ($E_{1/2}$ (**2a**/**2a**$^{+\cdot}$)) vs. Ag/0.1 M Ag$^+$ minus (0.74 – 0.68) V is equal to $E_{1/2}$ (**2a**/**2a**$^{+\cdot}$) vs. Ag/0.01 M Ag$^+$, which is estimated to be +1.42 V.

CIDNP Examination. A typical CIDNP examination of the photochemical reaction is as follows: suitable amounts (~10^{-3} M) of **1d** and **2b** were dissolved in acetonitrile-d_3 or in methanol-d_4 in a glass NMR sample tube. The sample was irradiated at room temperature under argon by a high-pressure Hg lamp through a glass filter (Toshiba UV-39) and the ^{1}H NMR signals were observed before, during, and after irradiation.

Photochemical Synthesis of Naphtho[1,2-*g*]quinoline-7,12-dione (9). A benzene solution (400 mL) of **8** (1 mmol) and a 1,1-diarylethylene (2 mmol) was irradiated at room temperature in the presence of pyridine (1 mmol) by a high-pressure Hg lamp (300 W). The amount of quinone consumed was followed by TLC. Starting quinone (**8**) was completely consumed within a half hour. The solution was further irradiated until the intermediate ethylene adduct disappeared (TLC). After several hours, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel and subsequent recrystallization.

Physical Properties of Naphtho[1,2-*g*]quinoxaline-7,12-diones. 5-Phenylnaphtho[1,2-*g*]quinoxaline-7,12-dione (9a): yellow needles (from hexane–chloroform); mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 9.71 (1 H, d, J = 8 Hz), 9.05 (1 H, d, J = 2 Hz), 9.01 (1 H, d, J = 2 Hz), 8.34 (1 H, s), 7.1–8.0 (8 H, m); IR (KBr) 1675 cm^{-1}; UV ($CHCl_3$) λ_{max} 265 nm (log ϵ 4.29), 323 (4.39), 434 (3.61); mass spectrum, m/e 336 (M$^+$). Anal. Calcd for $C_{22}H_{12}O_2N_2$: C, 78.56; H, 3.60; N, 8.33. Found: C, 78.47; H, 3.47; N, 8.41.

2-Methoxy-5-(*p*-methoxyphenyl)naphtho[1,2-*g*]-quinoxaline-7,12-dione (9b): red needles (from hexane–chloroform); mp 285.5–286.5 °C; ^{1}H NMR ($CDCl_3$) δ 9.26 (1 H, d, J = 2.5 Hz), 9.05 (1 H, d, J = 2 Hz), 9.01 (1 H, d, J = 2 Hz), 8.18 (1 H, s), 7.91 (1 H, d, J = 9.5 Hz), 7.42 (2 H, d, J = 9 Hz), 7.0–7.4 (1 H, m), 7.05 (2 H, d, J = 9 Hz), 4.04 (3 H, s), 3.90 (3 H, s); IR (KBr) 1675 cm^{-1}; UV ($CHCl_3$) λ_{max} 276 nm (log ϵ 4.38), 344 (4.22), 494 (3.78); mass spectrum, m/e 396 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_4N_2$: C, 72.72; H, 4.07; N, 7.07. Found: C, 72.74; H, 3.89; N, 6.89.

3-Methoxy-5-(*m*-methoxyphenyl)naphtho[1,2-*g*]-quinoxaline-7,12-dione (9c): orange needles (from hexane–chloroform); mp 241–242 °C; ^{1}H NMR ($CDCl_3$) δ 9.62 (1 H, d, J = 9 Hz), 9.05 (1 H, d, J = 2 Hz), 9.02 (1 H, d, J = 2 Hz), 8.30 (1 H, s), 7.0–7.5 (6 H, m), 3.88 (3 H, s), 3.79 (3 H, s); IR (KBr) 1670 cm^{-1}; UV ($CHCl_3$) λ_{max} 274 nm (log ϵ 4.17), 340 (4.39), 411 (3.72), 460 (3.58); mass spectrum, m/e 396 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_4N_2$: C, 72.72; H, 4.07; N, 7.07. Found: C, 72.64; H, 3.90; N, 7.11.

4-Methoxy-5-(*o*-methoxyphenyl)naphtho[1,2-*g*]-quinoxaline-7,12-dione (9d): red needles (from hexane–chloroform); mp 261–262 °C; ^{1}H NMR ($CDCl_3$) δ 9.31 (1 H, d, J = 8 Hz), 9.07 (1 H, d, J = 2 Hz), 9.01 (1 H, d, J = 2 Hz), 8.19 (1 H, s), 7.68 (1 H, t, J = 8.5 Hz), 7.1–7.4 (1 H, m), 7.05 (2 H, d, J = 8.5 Hz), 6.91 (2 H, d, J = 8.5 Hz), 3.63 (3 H, s), 3.49 (3 H, s); IR (KBr) 1675 cm^{-1}; UV ($CHCl_3$) λ_{max} 267 nm (log ϵ 4.47), 275 (4.47), 342 (4.26), 495 (3.49); mass spectrum, m/e 396 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_4N_2$: C, 72.72; H, 4.07; N, 7.07. Found: C, 72.76; H, 3.87; N, 6.98.

2-Methyl-5-(*p*-tolyl)naphtho[1,2-*g*]quinoxaline-7,12-dione (9e): yellow needles (from hexane–chloroform); mp >300 °C; ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, br s), 9.09 (1 H, d, J = 2 Hz), 9.04 (1 H, d, J = 2 Hz), 8.23 (1 H, s), 7.94 (1 H, d, J = 9 Hz), 7.1–7.6 (5 H, m), 2.66 (3 H, s), 2.50 (3 H, s); IR (KBr) 1675 cm^{-1}; UV ($CHCl_3$) λ_{max} 271 nm (log ϵ 4.31), 334 (4.31), 460 (3.67); mass spectrum, m/e 364 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_2N_2$: C, 79.11; H, 4.43; N, 7.69. Found: C, 78.91; H, 4.16; N, 7.39.

3-Methyl-5-(*m*-tolyl)naphtho[1,2-*g*]quinoxaline-7,12-dione (9f): yellow needles (from hexane–chloroform); mp 271–272 °C; ^{1}H NMR ($CDCl_3$) δ 9.66 (1 H, d, J = 9 Hz), 9.09 (1 H, d, J = 2 Hz), 9.05 (1 H, d, J = 2 Hz), 8.34 (1 H, s), 7.76 (1 H, br s), 7.65 (1 H, dd, J = 9, 2 Hz), 7.0–7.5 (4 H, m), 2.50 (6 H, s); IR (KBr) 1675 cm^{-1}; UV ($CHCl_3$) λ_{max} 265 nm (log ϵ 4.29), 333 (4.42), 392 (3.64), 444 (3.64); mass spectrum, m/e 364 (M$^+$). Anal. Calcd for $C_{24}H_{16}O_2N_2$: C, 79.11; H, 4.43; N, 7.69. Found: C, 79.02; H, 4.29; N, 7.45.

Registry No. **1a**, 26037-61-6; **1b**, 2065-37-4; **1c**, 13243-65-7; **1d**, 117-80-6; **1e**, 3129-39-3; **1f**, 58-27-5; **1g**, 2348-82-5; **2a**, 530-48-3; **2b**, 4356-69-8; **2c**, 1488-34-2; **2d**, 28358-60-3; **2e**, 2919-20-2; **2f**, 10605-48-8; **2g**, 6175-14-0; **2h**, 2642-81-1; **3a**, 72853-79-3; **3b**, 93403-91-9; **3c**, 93403-92-0; **3d**, 93403-93-1; **3e**, 93403-94-2; **4a**, 93403-95-3; **4b**, 93403-96-4; **4c**, 93403-97-5; **4d**, 93403-98-6; **4e** (X = Me, Y = Br), 93403-99-7; **4e′** (X = Br, Y = Me), 93404-00-3; **4f** (X = Me, Y = H), 93404-01-4; **4f′** (X = H; Y = Me), 93404-02-5; **4g**, 61705-19-9; **5a**, 54988-91-9; **5b**, 72735-91-2; **5c**, 93404-03-6; **5d**, 93404-04-7; **5e**, 93404-05-8; **5f**, 72853-75-9; **5g**, 93404-06-9; **5h**, 72735-93-4; **6a**, 93404-07-0; **6b**, 93404-08-1; **7a**, 93404-09-2; **7b**, 93404-10-5; **7c**, 93404-11-6; **7d**, 93404-12-7; **8**, 80672-66-8; **9a**, 93404-13-8; **9b**, 93404-14-9; **9c**, 93404-15-0; **9d**, 93404-16-1; **9e**, 93404-17-2; **9f**, 93404-18-3; **10**, 90020-53-4; **12**, 90020-54-5; **14**, 86927-80-2; **16**, 14151-20-3; **18a**, 116-11-0; **18b**, 109-92-2; **18c**, 111-34-2; **19a**, 108-22-5; **19b**, 108-05-4; **20** (R = R′ = Me), 93404-22-9; **20** (R = Et, R′ = H), 93404-23-0; **20** (R = *n*-Bu, R′ = H), 93404-24-1; **21** (R′ = Me), 93404-25-2; **21** (R′ = H), 93404-26-3; 1-phenyl-1-(2-furyl)ethylene, 75488-41-4; 1-phenyl-1-(2-thienyl)ethylene, 30616-74-1; 1-phenyl-1-(2-*N*-methylpyrrolyl)ethylene, 66643-66-1; 1-phenyl-1-(2-benzo[*b*]thienyl)-ethylene, 75488-49-2; 1-phenyl-1-(2-*N*-methylindolyl)ethylene, 66643-64-9; 1-phenyl-1-(3-pyridyl)ethylene, 74309-58-3; 1-phenyl-1-(4-pyridyl)ethylene, 54813-56-8; 4-phenylanthra[2,1-

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(45) Charlot, G. "Les Reactions Chimiques En Solution, L'Analyse Qualitative Minérale"; Japanese translation by Sone, K., Tanaka, M.; Kyoritsu Shuppan Co. Ltd.: Tokyo, 1974; pp 151.

b]furan-6,11-dione, 93404-27-4; 4-phenylanthra[2,1-*b*]thiophene-6,11-dione, 64747-11-1; 5-(2-thienyl)benz[*a*]anthracene-7,12-dione, 64747-12-2; 3-methyl-4-phenyl-3*H*-naphth[2,3-*e*]indole-6,11-dione, 66643-69-4; 8-phenylanthra[2,1-*d*]thiophene-8,13-dione, 75488-33-4; 5-(2-benzo[*b*]thienyl)benz[*a*]anthracene-7,12-dione, 75488-34-5; 5-methyl-6-phenyl-5*H*-naphtho[2,3-*c*]carbazole-8,13-dione, 66643-67-2; 5-(3-pyridyl)benz[*a*]anthracene-7,12-dione, 75488-37-8; 5-(4-pyridyl)benz[*a*]anthracene-7,12-dione, 75488-38-9; 2-methoxy-3-(2-methoxy-1-propenyl)-1,4-naphthoquinone, 93404-28-5; 2-bromo-3-(2-methoxy-1-propenyl)-1,4-naphthoquinone, 93404-29-6; 2-acetonyl-3-methoxy-1,4-naphthoquinone, 91406-82-5; 2-acetonyl-3-bromo-1,4-naphthoquinone, 91406-81-4; 6-methoxy-5,8-quinoxalinedione, 56369-10-9.

A Novel Hexacyclic Ring System from Glycoluril

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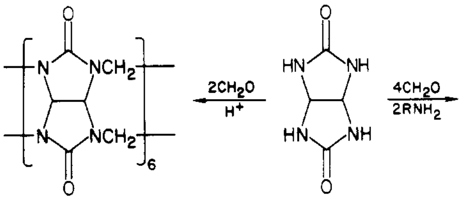
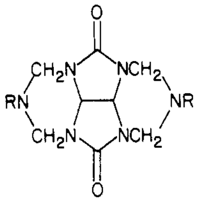
Condensation of 2 equiv of an alkanediamine (ethane–butane) with 6 equiv of formaldehyde and 1 equiv of glycoluril (or a simple derivative thereof) yields a new hexacyclic ring system. Seven examples are described (**4**–**10**). An X-ray crystallographic structure determination is provided.

Glycoluril (**1**) has proven to be a versatile progenitor of polycyclic ring systems. When allowed to react with formaldehyde under strongly acidic conditions, **1** yields the novel nonadecacyclic cage structure of cucurbituril (**2**).[2]



2 **1**



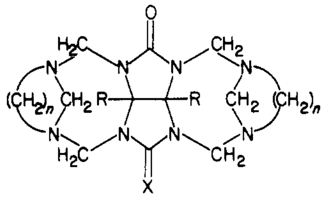
3

Under less stringent conditions **1** condenses with formaldehyde in the presence of aliphatic amines to yield **3**.[3] In attempting to carry out this latter reaction with certain alkanediamines, we have encountered yet another novel ring system, the subject of this report.

Results

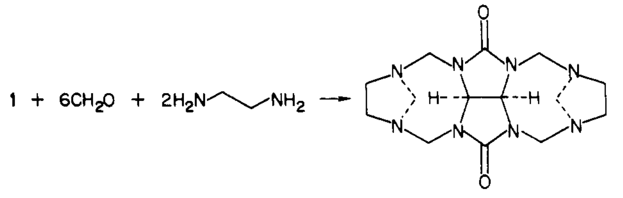
Synthesis. Slow addition of 1,2-ethanediamine to a refluxing mixture of **1** and formaldehyde in methanol yielded a high-melting crystalline substance **4**. The stoichiometry of the reaction was indicated to be **1** + $6CH_2O + 2H_2NCH_2CH_2NH_2 \rightarrow C_{14}H_{22}N_8O_2 + 6H_2O$ by mass spectral and NMR analyses of the product. An initially puzzling feature of the characterization of **4** was the clear indication that the six formaldehyde moieties had entered into two different and unique environments, according to NMR data (^1H, ^{13}C). However, elements of symmetry appeared to be present in the structure of **4**, since chemically equivalent carbons of the glycoluril and ethanediamine reactants retained magnetic equivalence in the product **4**. The spectral properties were eventually reconciled by the following equation.

Table I. Alkanediamine–Formaldehyde Condensation Products from Glycolurils



no.	X	R	*n*	M_r,[a] (MH$^+$)	yield, %
4	O	H	2	335	62
5	O	H	3	363	54
6	O	CH_3	2	363	28
7	O	CH_3	3	391	70
8	O	CH_3	4	419	40
9	O	C_6H_5	3		28
10	S	H	3	379	20

[a] FAB mass spectral molecular weight (Kratos MS-50, samples dissolved in glycerol–1% acetic acid on Cu probe, bombarded with 6 keV xenon atoms at 10^{-5} torr).



4

The new synthesis appears to have some generality. As may be seen in Table I, an analogous structure (**5**) was obtained employing 1,3-propanediamine and formaldehyde with **1**. The reaction succeeded equally well with substituted derivatives of the diurea component. Dimethylglycoluril and formaldehyde gave **6**, **7**, and **8** with 1,2-ethanediamine, 1,3-propanediamine, and 1,4-butanediamine, respectively. Diphenylglycoluril formed **9** with

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