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Lewis Acid-Mediated Addition of 1,2-Naphthoquinones with 1,1-Diarylethylenes and Photocyclization of the Adducts: A Facile Synthesis of 3,12-Disubstituted Chrysene-5,6-diones

Akio Takuwa,* Ikuo Kameoka, Akihisa Nagira,
Yutaka Nishigaichi, and Hidetoshi Iwamoto

Department of Chemistry, Faculty of Science, Shimane University, Nishikawatsu-cho, Matsue 690, Japan

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Polycyclic aromatic compounds have attracted much attention because of their physicochemical and biochemical properties.[1] In order to investigate the metabolism of carcinogenic polyaromatic hydrocarbons, a facile synthetic route to them is desirable. The Diels−Alder reaction[2] and photochemical cycloaddition reaction[3] between 1,4-naphthoquinones and 1,1-diarylethylenes or styrene derivatives have been very extensively developed as one of the promised syntheses of benz[*a*]anthracene-7,12-diones, which can be reduced to the corresponding polycyclic aromatic hydrocarbons. However, Gates reported that 1,2-naphthoquinone thermally added only to the very highly polarized 1,1-bis[*p*-(dimethylamino)phenyl]ethylene to give a conjugate addition product,[4] and we also reported that 1,2-naphthoquinone photochemically reacted as a heterodiene with 1,1-diphenylethylenes to give dihydrodioxins.[5] Thus, a synthetic method of chrysene-5,6-diones has not yet been developed in the reaction of 1,2-naphthoquinones with 1,1-diarylethylenes. Here we report that a convenient Lewis acid-promoted addition reaction between 1,2-naphthoquinones and 1,1-diarylethylenes and subsequent photocyclization of the addition products leads to the regioselective formation of 3,12-disubstituted chrysene-5,6-diones in excellent to good yields, which are the expected precursor of the corresponding aromatic hydrocarbons.

Addition Reactions of 1,1-Diarylethylenes to 1,2-Naphthoquinones. The addition reaction of 1,2-naphthoquinone (**1a**) with 1,1-diarylethylenes **2** except for the very highly polarized 1,1-bis[*p*-(dimethylamino)phenyl]ethylene (**2e**)[4] occurred in the absence of $BF_3\cdot OEt_2$. In contrast, the addition reaction of **2a**−**e** to **1a** smoothly proceeded in dichloromethane at −10 °C in the presence of $BF_3\cdot OEt_2$ to give the ethylene adducts, 4-(2,2-diarylethenyl)-1,2-naphthoquinones **6a**−**e**, in moderate to good yields except for the reaction between **1a** and **2b** (Scheme 1, Table 1). Other functionalized quinones, 3-chloro- (**1b**), 3-bromo- (**1c**), and 3-methoxy-1,2-naphthoquinone (**1d**), also reacted regioselectively with 1,1-diarylethylenes in the presence of $BF_3\cdot OEt_2$ to afford the corresponding ethylene adducts **6f**−**l**, in moderate to almost quantitative yields. Thus, the yields of **6** depended upon the nature of the substituents of both **1** and **2**. Among Lewis acids examined here, $BF_3\cdot OEt_2$ was the one of the best acids for the addition reaction listed in Table 1, but in the reactions of **1b** with **2b** and of **1d** with **2a**, $Ti(OPr^i)Cl_3$ was superior to other Lewis acids such as $BF_3\cdot OEt_2$, $TiCl_4$, or $Ti(OPr^i)_4$. However, the yields of **6a** and **6b** were not improved by using $TiCl_4$ or $Ti(OPr^i)Cl_3$ in the reactions of **1a** with **2a** or **2b** because 1,2-naphthoquinone **1a** decomposed in the presence of these Lewis acids under the present conditions.

Scheme 1

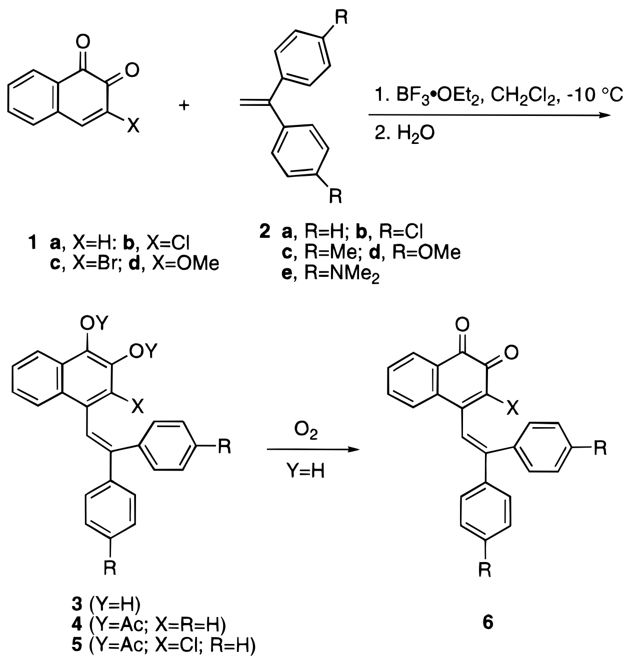

Table 1. BF_3-Promoted Addition Reaction of 1,2-Naphthoquinones with 1,1-Diarylethylenes[a]

quinone	ethylene	product	yield[b]/%
1a	**2a**	**6a**, X = H; R = H	58[c]
1a	**2b**	**6b**, X = H; R = Cl	6[c]
1a	**2c**	**6c**, X = H; R = Me	83
1a	**2d**	**6d**, X = H; R = OMe	95
1a	**2e**	**6e**, X = H; R = NMe_2	95
1b	**2a**	**6f**, X = Cl; R = H	96
1b	**2b**	**6g**, X = Cl; R = Cl	37 (61)[d,e]
1b	**2c**	**6h**, X = Cl; R = Me	97
1b	**2d**	**6i**, X = Cl; R = OMe	98
1b	**2e**	**6j**, X = Cl; R = NMe_2	98
1c	**2a**	**6k**, X = Br; R = H	97
1d	**2a**	**6l**, X = OMe; R = H	39[f] (88)[d]

[a] The reactions of **1** and **2** (1.3 equiv) were carried out in the presence of $BF_3\cdot OEt_2$ (1.5 equiv) in a dichloromethane solution at −10 °C under nitrogen atmosphere for 30 min. [b] Isolated yields. [c] When $TiCl_4$ or $Ti(OPr^i)Cl_3$ was used as a Lewis acid, the yield of the product was not improved. [d] Yields in parentheses refer to use of $Ti(OPr^i)Cl_3$ as a Lewis acid. [e] When $TiCl_4$ and $Ti(OPr^i)_4$ were used as Lewis acid, **6g** was obtained in 18 and 3% yields, respectively. [f] Two unidentified products were also formed.

The formation of ethylene adducts **6** can be rationalized as follows. Coordination of a Lewis acid to quinone carbonyl enhances the electrophilic character of the C-4 carbon in **1**[6] and facilities the nucleophilic attack of **2** on

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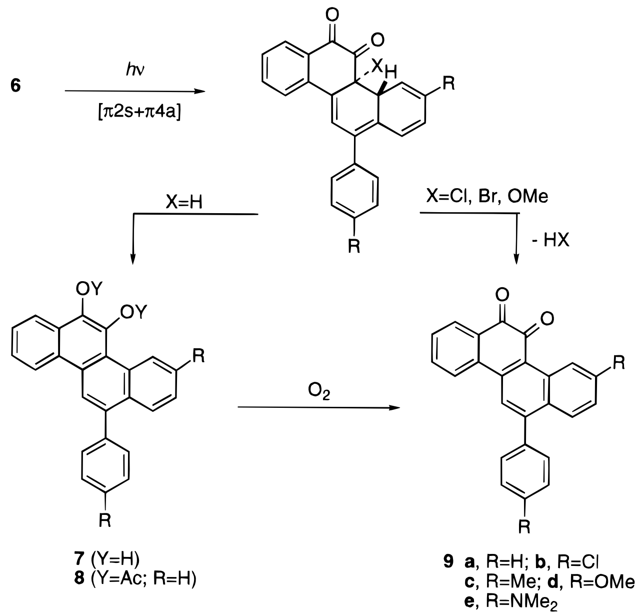
Scheme 2



that carbon. The resulting 2,5-cyclohexadienone intermediate may be deprotonated and enolize to afford the rather air-sensitive primary adduct, 4-substituted 1,2-naphthalenediols **3**, which are oxidized into the corresponding 1,2-quinones **6** during workup or isolating procedures. The diols **3** could be trapped as the diacetates **4** or **5** by treatment of the reaction mixture between **1a** or **1b** and **2a** with acetic anhydride−pyridine under nitrogen atmosphere (Scheme 1).

As can be seen in the $BF_3{\cdot}OEt_2$-mediated reactions (Table 1), the order of reactivities of para-disubstituted 1,1-diphenylethylenes **2a**−**e** toward **1a** increased in the order of electron-donating character of the substituent (**2e** > **2d** > **2c** > **2a** > **2b**). On the other hand, the nature of the substituent on quinones **1** could exert opposite influences on the yields of the ethylene adducts **6**. An electron-withdrawing substituent such as chloro or bromo enhances the electrophilic character of the C-4 carbon of **1b** or **1c** to give **6f** or **6k** in a very high yield, respectively, while the methoxy group diminishes the electrophilicity of that carbon to afford **6l** in a low yield.

Photocyclization of Ethylene Adducts to Chrysene-5,6-diones. When the ethylene adduct **6a** in an NMR sample tube ($CDCl_3$) was allowed to stand for 6 h in a laboratory, it was transformed partially into 12-phenylchrysene-5,6-dione (**9a**), but under dark conditions the cyclization product **9a** could not be detected by ^{1}H-NMR analysis. This clearly indicated that **6a** gradually cyclizes to **9a** even under a room light. This evidence prompted us to investigate the photocyclization reaction of **6**, which has the promising potential of a new convenient method for the synthesis of regioselectivity substituted chrysene-5,6-diones **9** (Scheme 2).

The ethylene adducts **6a**, **f**, **k**, **l** were irradiated independently in CH_3CN with a light (>300 nm) from a 300-W high-pressure Hg arc lamp for 2 h to give the same photocyclized product **9a** in 93, 95, 90, and 6% yields, respectively. The chrysene-5,6-dione (**9a**) could be formed via photochemical [π2s + π4a] cyclization[7] followed by enolization and air oxidation of the resulting diol **7** for **6a** (X = H) or followed by trans β-elimination of HX for **6f** (X = Cl), **6k** (X = Br), and **6l** (X = OMe) to be stabilized by aromatization (Scheme 2). The rather air-sensitive 1,2-diol intermediate **7** produced in the photocyclization processes of **6a** was trapped as diacetyl derivative **8** upon treatment of the irradiated mixture of **6a** with acetic anhydride−pyridine.

Table 2. Photocyclization of Ethylene Adducts 6[a]

		irradiatn time/h (product yield/%)[b]			
ethylene adduct	product	0.5	2	4	12
6f	**9a**	(38)	(97)		
6g	**9b**	(22)	(86)	(97)	
6h	**9c**	(40)	(80)	(96)	
6i	**9d**	(10)	(38)	(62)	(95)
6j	**9e**	(0)	(0)	(0)	(0)
6j	**9e**			(97)[c]	

[a] Irradiation was carried out in an acetonitrile solution (10 mL) of **6** (0.1 mmol). [b] Yields were determined by ^{1}H-NMR. [c] Irradiation was carried out in the presence of trifluoroacetic acid.

From an organic synthetic point of view, we examined the photochemical cyclizations of ethylene adducts **6f**−**j** because they were obtained in good to almost quantitative yields from the Lewis acid-promoted addition reaction of 3-chloro-1,2-naphthoquinone **1b** with **2a**−**e** as shown in Table 1. The results are summarized in Table 2. All of the ethylene adducts except for **6i** and **6j** produced the corresponding polycyclic aromatic quinones **9a**−**c** in very high yields (>95%) upon irradiation for 2−4 h. A longer irradiation (12 h) was required for complete transformation of **6i** to **9d**. Thus, the photocyclization reaction tends to be depressed by the electron-donating substituent in the 1,1-diphenylethenyl moiety of the ethylene adducts.

In contrast to these ethylene adducts, no cyclization reaction occurred in the irradiation of 3-chloro-4-[2,2-bis(*p*-dimethylamino)phenyl]-1,2-naphthoquinone (**6j**). However, when irradiation of **6j** was carried out in the presence of trifluoroacetic acid, the corresponding chrysene-5,6-dione **9e** was obtained in a very high yield as shown in Table 2. In the presence of a large excess (100 equiv) of trifluoroacetic acid, a broad electronic absorption maximum of **6j** probably due to intramolecular charge-transfer band shifted from 610 (ϵ_{max} 9250) to 425 nm (ϵ_{max} 600) in acetonitrile, where the protonation probably occurred on the nitrogen atom of the electron-releasing dimethylamino group.[8] As a result of loss of the strongly electron-donating ability of the dimethylamino group by the protonation, the photocyclization of **6j** came to proceed to give **9e**. Thus, the desired 3,12-disubstituted chrysene-5,6-diones **9a**−**e** could be obtained in very high yields by photochemical intramolecular cyclization of the ethylene adducts **6f**−**j**.

The chrysene-5,6-diones **9a** and **9c** were reduced by lithium aluminum hydride to the corresponding aromatic hydrocarbons such as **10** and **11**. Likewise, they were converted to the diacetoxy derivatives **8** and **12** by reductive acetylation with zinc−acetic anhydride.

Experimental Section

All 1,2-naphthoquinones **1a**,[9] **1b**,[10] **1c**,[11] and **1d**[12] were prepared by the methods described in the literature. 1,1-Diarylethylenes were commercially available and/or synthesized

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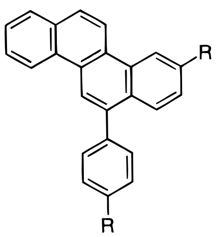
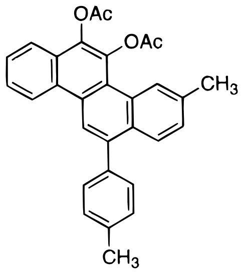


10 (R=H)
11 (R=CH_3)



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by using the method of Allen et al.[13] Dichloromethane and acetonitrile were distilled from calcium hydride. The Lewis acids were commercially available and used without further purifications. The ^{1}H-NMR and ^{13}C-NMR spectra were run in chloroform-*d* and measured on a 270 MHz instrument. Satisfactory analytical data (±0.4% for C, H, N) were obtained for all new compounds.

General Procedure for the Addition Reaction. To a dichloromethane solution (20 mL) of **1** (0.5 mmol) was added a Lewis acid (1.5 mmol) under N_2 at −10 °C. After a few minutes, **2** (0.6 mmol) was added dropwise, and the reaction mixture was stirred for 0.5 h at that temperature. The reaction mixture was quenched with a saturated aqueous ammonium chloride solution and then extracted with ether. The combined organic extracts were washed with water followed by brine and dried over anhydrous sodium sulfate. Evaporation of the solvent gave the residue, which was purified by column chromatography over silica gel (eluent: hexane−ether mixture) to yield the crude ethylene adducts **6**, which were further purified by TLC or recrystallization and identified by their physical and spectral characteristics.

Physical Properties of the Ethylene Adducts. 4-(2,2-Diphenylethenyl)-1,2-naphthoquinone (6a): orange red crystals (from benzene−hexane); mp 193−195 °C; ν_{max} 1695, 1655 cm^{-1}; δ_H 6.06 (1H, d, $J = 1.2$ Hz), 6.91 (1H, d, $J = 1.2$ Hz), 7.14−7.70 (8H, m), 7.39 (5H, s), 8.14 (1H, dd, $J = 7.5$, 1.2 Hz); δ_C 122.6, 127.4, 128.0, 128.4 (×2), 128.6 (×2), 128.7 (×2), 128.8 (×2), 129.1, 129.7 (×2), 130.1, 130.8,, 131.5, 135.4, 135.6, 138.7, 141.8, 151.0, 152.7, 179.2, 180.4; MS *m/z* 336 (M$^+$).

4-[2,2-Bis(*p*-chlorophenyl)ethenyl]-1,2-naphthoquinone (6b): orange red crystals (from benzene−hexane); mp 182−184 °C; ν_{max} 1695, 1660 cm^{-1}; δ_H 6.06 (1H, d, $J = 1.2$ Hz), 6.89 (1H, d, $J = 1.2$ Hz), 7.07−7.67 (11H, m), 8.16 (1H, dd, $J = 7.5$, 1.2 Hz); MS *m/z* 404 (M$^+$).

4-(2,2-Di-*p*-tolylethenyl)-1,2-naphthoquinone (6c): red crystals (from benzene−hexane); mp 173−174 °C; ν_{max} 1685, 1650 cm^{-1}; δ_H 2.32 (3H, s), 2.41 (3H, s), 6.06 (1H, s), 6.84 (1H, s), 7.05−7.71 (11H, m), 8.12 (1H, d, $J = 7.6$ Hz); MS *m/z* 364 (M$^+$).

4-[2,2-Bis(*p*-methoxyphenyl)ethenyl]-1,2-naphthoquinone (6d): red oil; ν_{max} 1695, 1660 cm^{-1}; δ_H 3.79 (3H, s), 3.86 (3H, s), 6.09 (1H, d, $J = 1.2$ Hz), 6.76 (1H, d, $J = 1.2$ Hz), 6.79 (2H, d, $J = 8.8$ Hz), 6.91 (2H, d, $J = 8.8$ Hz), 7.09 (2H, d, $J = 8.8$ Hz), 7.32 (2H, d, $J = 8.8$ Hz), 7.49−7.73 (3H, m), 8.14 (1H, dd, $J = 7.6$, 1.5 Hz); MS *m/z* 396 (M$^+$).

4-[2,2-Bis[*p*-(dimethylamino)phenyl]ethenyl]-1,2-naphthoquinone (6e): physical and spectroscopic properties agreed with the data reported in ref 4.

3-Chloro-4-(2,2-diphenylethenyl)-1,2-naphthoquinone (6f): orange red crystals (from benzene); mp 181−182 °C; ν_{max} 1665 cm^{-1}; δ_H 6.76 (1H, s), 7.12−7.57 (13H, m), 8.14 (1H, dd, $J = 7.3$, 1.2 Hz); δ_C 120.6, 128.3 (×2), 128.6 (×4), 129.0, 129.1, 129.2, 129.4 (×2), 130.1, 130.4, 130.5, 131.0, 133.9, 135.5, 139.1, 141.0, 149.9, 150.6, 174.3, 177.8.

3-Chloro-4-[2,2-bis(*p*-chlorophenyl)ethenyl]-1,2-naphthoquinone (6g): orange red crystals (from benzene−hexane); mp 205−208 °C; ν_{max} 1690, 1670 cm^{-1}; δ_H 6.73 (1H, s), 7.05−7.53 (11H, m), 8.09 (1H, d, $J = 7.1$ Hz); MS *m/z* 438 (M$^+$), 440 (M + 2), 442 (M + 4).

3-Chloro-4-(2,2-*p*-ditolylethenyl)-1,2-naphthoquinone (6h): orange crystals (from benzene); mp 164−166 °C; ν_{max} 1670 cm^{-1}; δ_H δ 2.24 (3H, s), 2.41 (3H, s), 6.68 (1H, s), 7.00 (4H, q, $J = 8.1$ Hz), 7.21 (2H, d, $J = 7.8$ Hz), 7.34 (2H, d, $J = 7.8$ Hz), 7.38−7.56 (3H, m), 8.03 (1H, dd, $J = 7.5$, 1.7 Hz); MS *m/z* 398 (M$^+$).

3-Chloro-4-[2,2-bis(*p*-methoxyphenyl)ethenyl]-1,2-naphthoquinone (6i): red crystals (from benzene−hexane); mp 145−146 °C; ν_{max} 1695, 1670 cm^{-1}; δ_H 3.73 (3H, s), 3.87 (3H, s), 6.63 (1H, s), 6.69 (2H, d, $J = 8.8$ Hz), 6.93 (2H, d, $J = 8.8$ Hz), 7.07 (2H, d, $J = 8.8$ Hz), 7.34−7.53 (5H, m), 8.03 (1H, dd, $J = 7.3$, 1.7 Hz); δ_C 55.2, 55.5, 113.7 (×2), 113.9 (×2), 118.5, 128.4 (×2), 129.2, 130.1 (×2), 130.2, 130.3, 131.1 (×2), 131.9, 133.8, 134.1, 135.3, 150.4, 150.5, 160.2, 160.6, 174.5, 178.2; MS *m/z* 430 (M$^+$).

3-Chloro-4-[2,2-bis[*p*-(dimethylamino)phenyl]ethenyl]-1,2-naphthoquinone (6j): violet blue crystals (from benzene−hexane); mp 238−242 °C; ν_{max} 1696, 1661, 1604, 1523, 1361, 1192, 824 cm^{-1}; δ_H 2.89 (6H, s), 3.03 (6H, s), 6.43 (2H, d, $J = 8.8$ Hz), 6.57 (1H, s), 6.71 (2H, d, $J = 9.0$ Hz), 7.01 (2H, d, $J = 9.0$ Hz), 7.23−7.47 (5H, m), 7.95−7.98 (1H, m); MS *m/z* 456 (M$^+$).

3-Bromo-4-(2,2-diphenylethenyl)-1,2-naphthoquinone (6k): red needles (from benzene−hexane); mp 195−198 °C; ν_{max} 1670 cm^{-1}; δ_H 6.72 (1H, s), 7.14−7.57 (13H, m), 8.14 (1H, dd, $J = 6.8$, 1.4 Hz); MS *m/z* 414 (M$^+$), 416 (M$^+$).

4-(2,2-Diphenylethenyl)-3-methoxy-1,2-naphthoquinone (6l): dark red prisms (from hexane−benzene); mp 130−132 °C; ν_{max} 1696, 1662, 1562, 1334, 1188 cm^{-1}; δ_H 3.55 (3H, s), 6.64 (1H, s), 7.16−7.50 (13H, m), 7.97 (1H, dd, $J = 8.1$, 1.5 Hz); MS *m/z* 366 (M$^+$).

Trapping of the Ethylene Adducts as Acetyl Derivatives. The addition reaction of **1a** (39.5 mg, 0.25 mmol) with **2a** (68 mg, 0.37 mmol) in the presence of $BF_3{\cdot}OEt_2$ was undertaken according to the general procedure described above. The treatment of the reaction mixture with acetic anhydride−pyridine gave 1,2-diacetoxy-4-(2,2-diphenylethenyl)naphthalene **4** (63 mg) as prisms (from methanol): mp 173−175 °C; δ_H 2.18 (3H, s), 2.42 (3H, s), 6.85 (1H, s), 7.07−7.56 (13H, m), 7.82 (1H, dd, $J = 7.6$, 1.7 Hz), 8.15 (1H, dd, $J = 6.6$, 1.9 Hz); ν_{max} 1770, 1371, 1208, 1154, 767 cm^{-1}; MS *m/z* 442 (M$^+$), 380 [M − ($CH_2{=}C{=}O$)], 338 [M − 2($CH_2{=}C{=}O$)].

Similar treatment of the reaction mixture of **1b** (48 mg) and **2a** with acetic anhydride−pyridine afforded 3-chloro-1,2-diacetoxy-4-(2,2-diphenylethenyl)naphthalene (**5**) (89 mg) as prisms (from methanol−benzene): mp 221−223 °C; δ_H 2.34 (3H, s), 2.42 (3H, s), 6.97−7.05 (6H, m), 7.34−7.50 (7H, m), 7.70 (1H, d, $J = 7.1$ Hz), 7.99 (1H, d, $J = 7.8$ Hz); δ_C 20.3, 20.4, 121.4, 122.3, 126.0, 126.1, 126.2, 126.9 (×2), 127.6, 127.8 (×2), 128.2, 128.3 (×2), 128.4 (×2), 129.6 (×2), 130.3, 133.7, 136.4, 137.9, 139.3, 142.3, 148.1, 167.5, 167.9; ν_{max} 1773, 1369, 1198, 1151, 766, 700 cm^{-1}; MS *m/z* 456 (M$^+$), 414 [M − ($CH_2{=}C{=}O$)], 372 [M − 2($CH_2{=}C{=}O$)].

General Procedure for Photochemical Cyclization Reaction of the Ethylene Adducts 6. An acetonitrile solution (10 mL) of an ethylene adduct **6** (0.1 mmol) was irradiated at room temperature under N_2 by a high-pressure Hg arc lamp (300 W). The amount of the ethylene adduct consumed was followed by TLC. After the complete consumption of the ethylene adduct, the reaction mixture was concentrated in vacuo to give crude **9**, which was further purified by recrystallization or preparative TLC on silica gel. In the case of the photochemical cyclization reaction of **6j**, irradiation was carried out in the presence of a large excess (100 equiv) of trifluoroacetic acid.

Physical Properties of the Cyclization Products. 12-Phenylchrysene-5,6-dione (9a): orange red needles (from benzene−hexane); mp 245−247 °C; δ_H 7.46−7.74 (9H, m), 7.86 (1H, d, $J = 7.8$ Hz), 8.03 (1H, s), 8.10 (1H, d, $J = 7.8$ Hz), 8.17 (1H, dd, $J = 7.8$, 1.5 Hz), 9.50 (1H, d, $J = 8.8$ Hz); ν_{max} 3070, 3050, 1685, 1665, 1590, 1480, 1410, 1300, 760 cm^{-1}; MS *m/z* 334 (M$^+$).

3-Chloro-12-(*p*-chlorophenyl)chrysene-5,6-dione (9b): red crystals; mp 268−270 °C; δ_H 7.41−7.79 (8H, m), 7.99 (1H, s), 8.08 (1H, d, $J = 7.6$ Hz), 8.17 (1H, dd, $J = 7.6$, 1.5 Hz), 9.56 (1H, d, $J = 2.2$ Hz); MS *m/z* 402 (M$^+$), 404 (M + 2), 406 (M + 4).

3-Methyl-12-*p*-tolylchrysene-5,6-dione (9c): red needles (benzene); mp 195−197 °C; δ_H 2.50 (3H, s), 2.57 (3H, s), 7.30−7.50 (6H, m), 7.69 (1H, dt, $J = 7.6$, 1.5 Hz), 7.78 (1H, d, $J = 8.8$ Hz), 7.93 (1H, s), 8.07 (1H, d, $J = 7.6$ Hz), 8.15 (1H, dd, $J = 7.6$,

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(13) Allen, C. F. H.; Converse, S. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 226.

1.5 Hz), 9.31 (1H, s); $\nu_{\max}$ 1690, 1670, 1590, 1360, 1300, 830, 765 cm^{-1}; MS m/z 362 (M^+).

3-Methoxy-12-(*p*-methoxyphenyl)chrysene-5,6-dione (9d): red prisms (benzene−hexane); mp 253−255 °C; δ_H 3.91 (3H, s), 4.03 (3H, s), 7.08−7.51 (6H, m), 7.71 (1H, dt, J = 8.1, 1.5 Hz), 7.81 (1H, d, J = 9.3 Hz), 7.89 (1H, s), 8.11 (1H, d, J = 8.1 Hz), 8.18 (1H, dd, J = 8.1, 1.5 Hz), 9.14 (1H, dd, J = 8.1, 2.7 Hz); $\nu_{\max}$ 1686, 1649, 1610, 1581, 1244, 1217 cm^{-1}; MS m/z 394 (M^+).

3-(Dimethylamino)-12-[*p*-(dimethylamino)phenyl]chrysene-5,6-dione (9e): dark blue needles; mp >300 °C; δ_H 3.10 (6H, s), 3.20 (6H, s), 6.88 (2H, d, J = 9.0 Hz), 7.06 (1H, dd, J = 9.3, 2.4 Hz), 7.43 (1H, t, J = 7.8 Hz), 7.45 (2H, d, J = 9.0 Hz), 7.66 (1H, dt, J = 7.8, 1.5 Hz), 7.72 (1H, s), 7.87 (1H, d, J = 9.3 Hz), 8.09 (1H, d, J = 7.8 Hz), 8.16 (1H, dd, J = 7.8, 1.5 Hz), 8.99 (1H, d, J = 2.4 Hz); $\nu_{\max}$ 1680, 1640, 1608, 1562, 1360, 1334, 1188, 818 cm^{-1}; MS m/z 420 (M^+).

Trapping of 12-Phenylchrysene-5,6-diol (7) as Acetyl Derivatives. After irradiation of **6a** in acetonitrile under N_2, acetic anhydride and pyridine were added to the irradiated mixture. Usual workup afforded 5,6-diacetoxy-12-phenylchrysene (**8**) in 70% yield, whose physical properties were described below.

Reduction of Chrysene-5,6-diones to the Corresponding Aromatic Hydrocarbons. A tetrahydrofuran solution (20 mL) of **9a** or **9c** (0.1 mmol) and an excess amount (ca. 10 equiv) of lithium aluminum hydride was refluxed for 12 h. After hydrolysis, the reaction mixture was chromatographed on silica gel to give the corresponding aromatic hydrocarbon.

Physical Properties of Aromatic Hydrocarbons. 6-Phenylchrysene (10): pale yellow crystals; mp 102−105 °C; yield 27%; δ_H 7.47−7.75 (9H, m), 7.99−8.05 (3H, m), 8.65 (1H, s), 8.75 (1H, d, J = 8.9 Hz), 8.77 (1H, d, J = 8.7 Hz), 8.88 (1H, d, J = 8.9 Hz); $\nu_{\max}$ 1590, 1440, 1240, 820, 778, 762, 703 cm^{-1}; MS m/z 304 (M^+).

3-Methyl-12-*p*-tolylchrysene (11): white crystals; mp 45−49 °C; yield 23%; δ_H 2.51 (3H, s), 2.68 (3H, s), 7.34 (2H, d, J = 8.1 Hz), 7.33−7.43 (1H, m), 7.53 (2H, d, J = 8.1 Hz), 7.57−7.71 (2H, m), 7.93 (1H, d, J = 8.5 Hz), 8.01 (2H, d, J = 8.5 Hz), 8.57 (1H, s), 8.65 (1H, s), 8.77 (2H, d, J = 8.9 Hz); δ_C 29.4, 29.7, 121.2, 121.3, 123, 123.2, 126.6, 126.9, 127.0, 127.4, 128.2 (d), 128.5, 128.8, 129.0, 129.1, 129.2, 130.1 (×2), 130.6, 131.1, 132.2, 136.2, 137.1, 138.5, 139.2; $\nu_{\max}$ 2919, 1620, 1506, 1435 824, 763 cm^{-1}; MS m/z 332 (M^+).

Reductive Acetylation of Chrysene-5,6-diones. Chrysene-5,6-dione **9a** and **9c** (0.2 mmol) and an excess amount of zinc powder were added to acetic anhydride (2 mL). After the reaction mixture was refluxed for 30 min, the reaction mixture was hydrolyzed and neutralized with an aqueous solution of sodium carbonate. The corresponding diacetate **8** or **12** was extracted with ether and purified by recrystallization.

Physical Properties of Diacetates. 5,6-Diacetoxy-12-phenylchrysene (8): needles (from ethanol−benzene); yield 84%; mp 251−252 °C; δ_H 2.55 (3H, s), 2.57 (3H, s), 7.50−7.73 (9H, m), 7.93−8.01 (2H, m), 8.63 (1H, s), 8.76−8.80 (1H, m), 9.25 (1H, d, J = 9.2 Hz); $\nu_{\max}$ 1773, 1368, 1201, 1098, 760 cm^{-1}; MS m/z 420 (M^+), 378 [$M - (CH_2{=}C{=}O)$], 336 [$M - 2(CH_2{=}C{=}O)$].

5,6-Diacetoxy-3-methyl-12-*p*-tolylchrysene (12): pale yellow needles (from ethanol−benzene); yield 70%; mp 235−237 °C; δ_H 2.50 (3H, s), 2.54 (3H, s), 2.56 (3H, s), 2.60 (3H, s), 7.35 (2H, d, J = 8.0 Hz), 7.36−7.40 (1H, m), 7.48 (2H, d, J = 8.0 Hz), 7.64−7.71 (2H, m), 7.89−7.95 (2H, m), 8.55 (1H, s), 8.74−8.77 (1H, m), 9.04 (1H, s); $\nu_{\max}$ 1778, 1367, 1198, 1182, 828, 763 cm^{-1}; MS m/z 448 (M^+), 406 [$M - (CH_2{=}C{=}O)$], 364 [$M - 2(CH_2{=}C{=}O)$].

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