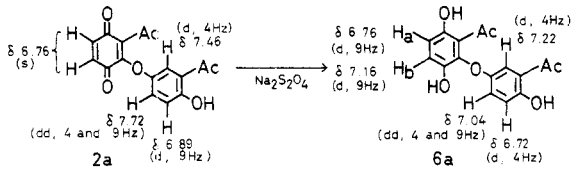

Figure 5. Reduction of **2a** with sodium hydrosulfite afforded 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-dihydroxybenzene (**6a**).

alkoxy-1,4-benzoquinones appeared as a singlet at δ 6.73–6.68.[10]

For confirmation of the structure of **2a**, reduction with sodium hydrosulfite was carried out. A solution of sodium hydrosulfite (60 mg, 0.35 mmol) in water (20 mL) was added to a stirred solution of **2a** (50 mg, 0.17 mmol) in ether (50 mL). After the mixture was stirred at room temperature for 30 min, the color of the organic phase was changed from red to yellow. The ethereal phase was washed with water, dried over magnesium sulfate, and concentrated to yield 2-acetyl-3-(3-acetyl-4-hydroxyphenoxy)-1,4-dihydroxybenzene (**6a**) in 80% yield (Figure 5). The ^{1}H NMR spectrum of **6a** showed two doublets at δ 6.76 and 7.16 (J = 9 Hz), due to the aromatic protons H_a and H_b (solvent CD_3CN). This result clearly indicates the presence of two groups of vicinal hydrogens.

Photolysis of 2-acetyl-5-methyl-1,4-benzoquinone (**1b**) in the presence of rose bengal afforded the dimer 2-acetyl-5-methyl-3-(3-acetyl-6-methyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2b**): 60% yield; red needles; mp 134.0–135.0 °C; UV_{max} (CH_3CN) 480 nm (sh, ϵ 306), 340 (4240), 260 (26600), 226 (22000); IR (KBr disk) 3320 (OH), 1700, 1670, 1650 (C=O), 1182 cm^{-1} (O); NMR ($CDCl_3$) δ 2.08 (d, 3, J = 2 Hz), 2.32 (s, 3), 2.36 (s, 3), 2.56 (s, 3), 6.64 (q, 1, J = 2 Hz), 6.88 (s, 1), 7.22 (s, 1), 11.64 (s, 1, OH). Anal. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 4.91. Found: C, 65.70; H, 4.92.

When 2-propanoyl-5-methyl-1,4-benzoquinone (**1c**) was used, 2-propanoyl-5-methyl-3-(3-propanoyl-6-methyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2c**) was obtained: 55% yield; red crystals; mp 124.0–125.0 °C; NMR ($CDCl_3$) δ 1.02 (t, 3, J = 8 Hz), 1.20 (t, 3, J = 8 Hz), 2.08 (d, 3, J = 2 Hz), 2.34 (s, 3), 2.61 (q, 2, J = 8 Hz), 2.92 (q, 2, J = 8 Hz), 6.66 (q, 1, J = 2 Hz), 6.90 (s, 1), 7.28 (s, 1), 11.72 (s, 1, OH). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.14; H, 5.79.

When 2-butanoyl-5-methyl-1,4-benzoquinone (**1d**) was irradiated in the presence of rose bengal, the quinone dimer 2-butanoyl-5-methyl-3-(3-butanoyl-6-methyl-4-hydroxyphenoxy)-1,4-benzoquinone (**2d**) was obtained: 50% yield; yellow needles; mp 109.0–110.0 °C; IR (KBr disk) 3320 (OH), 1700, 1650 (C=O), 1180 cm^{-1} (O); NMR ($CDCl_3$) δ 0.88 (t, 3, J = 8 Hz), 0.98 (t, 3, J = 8 Hz), 1.58 (sext, 2, J = 8 Hz), 1.72 (sext, 2, J = Hz), 2.04 (d, 3, J = 1.5 Hz), 2.32 (s, 3), 2.54 (t, 2, J = 8 Hz), 2.82 (t, 2, J = 8 Hz), 6.60 (q, 1, J = 1.5 Hz), 6.82 (s, 1), 7.18 (s, 1), 11.78 (s, 1, OH). Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.73; H, 6.29. Found: C, 68.67; H, 6.50.

Photolysis of 2-(2-methylpropanoyl)-5-methyl-1,4-benzoquinone (**1e**) afforded 2-(2-methylpropanoyl)-5-methyl-3-[3-(2-methylpropanoyl)-6-methyl-4-hydroxyphenoxy]-1,4-benzoquinone (**2e**): 40% yield; red needles; mp 115.0–116.0 °C; IR (KBr disk) 3320 (OH), 1700, 1650 (C=O), 1185 cm^{-1} (O); NMR ($CDCl_3$) δ 1.16 (d, 6, J = 8 Hz), 1.18 (d, 6, J = 8 Hz), 2.02 (d, 3, J = 1.5 Hz), 2.32 (s, 3), 2.84 (q, 1, J = 8 Hz), 3.36 (q, 1, J = 8 Hz), 6.60 (q, 1, J = 1.5 Hz), 6.84 (s, 1), 7.14 (s, 1), 12.28 (s, 1, OH). Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.73; H, 6.29. Found: C, 68.58; H, 6.44.

When an acetonitrile solution of 2-(carbomethoxy)-1,4-benzoquinone (**4a**) in the presence of rose bengal was irradiated, the quinone dimer 2-(carbomethoxy)-3-[3-(carbomethoxy)-4-hydroxyphenoxy]-1,4-benzoquinone (**5a**) was obtained: 42% yield; red-yellow needles; mp 150.0–151.0 °C; UV_{max} (CH_3CN) 480 nm (sh, ϵ 250), 370 (sh, 1200), 320 (4460), 250 (sh, 16700), 240 (18100), 214 (28900); NMR ($CDCl_3$) δ 3.68 (s, 3), 4.00 (s, 3), 6.88 (s, 2), 7.02 (d, 1, J = 10 Hz), 7.30 (dd, 1, J = 10 and 4 Hz), 7.58 (d, 1, J = 4 Hz), 10.56 (s, 1, OH).

When 2-(carboethoxy)-1,4-benzoquinone (**4b**) was irradiated, the dimer 2-(carboethoxy)-3-[3-(carboethoxy)-4-hydroxyphenoxy]-1,4-benzoquinone (**5b**) was obtained: 40% yield; yellow needles; mp 92.0–93.0 °C; UV_{max} (CH_3CN) 480 nm (sh, ϵ 252), 370 (sh, 1130), 298 (4580), 250 (sh, 16300), 242 (18000), 214 (28200); NMR ($CDCl_3$) δ 1.20 (t, 3, J = 8 Hz), 1.40 (t, 3, J = 8 Hz), 4.06 (q, 2, J = 8 Hz), 4.40 (q, 2, J = 8 Hz), 6.78 (s, 2), 6.92 (d, 1, J = 9 Hz), 7.20 (dd, 1, J = 9 and 4 Hz), 7.70 (d, 1, J = 4 Hz), 10.70 (s, 1, OH).

1,4-Benzoquinone, 2-methyl-1,4-benzoquinone, 2-chloro-1,4-benzoquinone, and 2-bromo-1,4-benzoquinone were stable under the irradiated conditions in the presence of rose bengal and were recovered almost quantitatively.

Registry No. **1a**, 1125-55-9; **1b**, 63076-94-8; **1c**, 65781-68-2; **1d**, 72926-14-8; **1e**, 72926-15-9; **2a**, 68157-88-0; **2b**, 72926-16-0; **2c**, 72926-17-1; **2d**, 72926-18-2; **2e**, 72926-19-3; **4a**, 3958-79-0; **4b**, 62830-98-2; **5a**, 72857-89-7; **5b**, 72926-20-6; **6a**, 72926-21-7; α-pinene, 80-56-8; *trans*-3-hydroxypin-2(10)-ene, 1674-08-4.

Facile Photochemical Synthesis of Polycyclic Aromatic Compounds[1]

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A variety of polycyclic aromatic quinones, which are easily reduced to the corresponding aromatic hydrocarbons, were synthesized via a one-pot photocycloaddition reaction of simple 2-halogenated 1,4-naphthoquinone derivatives with 1,1-disubstituted ethylenes. The yields of the photocycloadditions are generally fairly good.

7,12-Dimethylbenz[*a*]anthracene is one of the most potent carcinogenic compounds known, and many efforts to synthesize polycyclic aromatic hydrocarbons and their heteroatom analogues have concentrated on attempts to elucidate the correlation between structure and carcinogenic activity. One basic synthetic approach to polycyclic aromatic hydrocarbons such as benz[*a*]anthracene depends on step-by-step construction of the carbon skeleton involving, for example, Friedel–Crafts acylation followed by Clemmensen reduction or Elbs condensation.[2] However, these procedures are laborious, and the overall yields are generally poor.

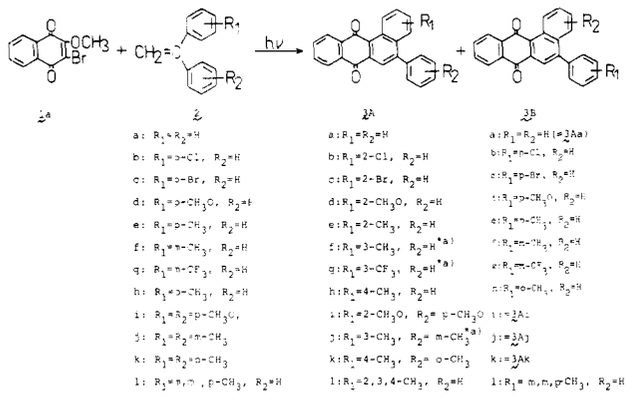
A one-pot synthesis of the carbon skeleton of benz[*a*]anthracenes was disclosed recently by Manning et al.[3]

(1) (a) K. Maruyama and T. Otsuki, *Chem. Lett.*, 87 (1975); (b) K. Maruyama, T. Otsuki, and K. Mitsui, *Bull. Chem. Soc. Jpn.*, **43**, 3361 (1976); (c) K. Maruyama, K. Mitsui, and T. Otsuki, *Chem. Lett.*, 853 (1977); (d) *ibid.*, 323 (1978).

(2) Cf.: G. M. Badger and J. W. Cook, *J. Chem. Soc.*, 802 (1939); J. L. Wood and L. F. Fieser, *J. Am. Chem. Soc.*, **73**, 4491 (1951); M. S. Newman, V. Sankaran, and D. R. Olson, *ibid.*, **98**, 3237 (1976); W. Girke and E. D. Bergmann, *Chem. Ber.*, **109**, 1038 (1976).

0022-3263/80/1945-1424$01.00/0

Scheme I

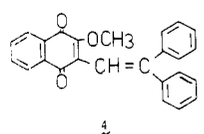


*a: 1-Substituted isomer was also identified in a trace amount.

Using the Diels–Alder reaction of 1,4-naphthoquinone with styrene derivatives, they constructed the carbon skeleton of benz[*a*]anthracene-7,12-diones. However, in spite of its convenience and the improved yield, several days at high temperature are required to complete the Diels–Alder reaction. Moreover, this procedure may have a limitation for controlling the regioselectivity in the condensation reaction, especially when the ring-substituted 1,4-naphthoquinones are employed.

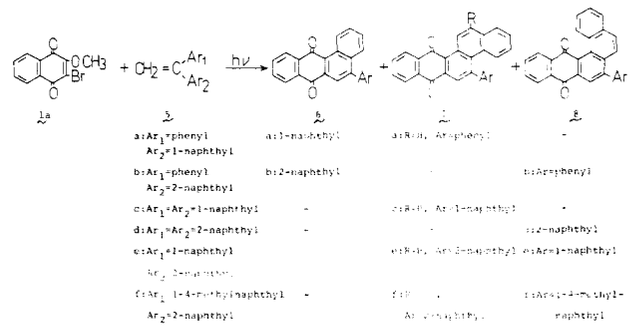
We now wish to report a convenient and time-saving one-pot photocycloaddition reaction leading to the formation of polycyclic aromatic quinones or hydrocarbons. In this manner an important class of key intermediates to polycyclic aromatic compounds, i.e., quinones and hence hydrocarbons, may be obtained in fairly good yields under mild conditions, starting from simple 2-halogenated quinones and 1,1-disubstituted ethylenes.

The photocycloaddition reaction is illustrated in Scheme I which exemplifies the synthesis of benz[*a*]anthracene-7,12-diones. On irradiation of a benzene solution of 2-bromo-3-methoxy-1,4-naphthoquinone (1 mmol) and 1,1-diarylethylene (2 mmol) with a high-pressure Hg arc lamp (300 W), the yellow color of the solution gradually turned red. The photochemical reaction was complete within several hours (5–12 h) at room temperature and gave benz[*a*]anthracene-7,12-dione derivatives in yields of 9–68% after purification by column chromatography. Benzene or benzene–hexane (1/1) was the best solvent system for the photocycloaddition reaction. Although the same products were obtained in ethanol, ether, ethyl acetate, or chloroform, the yield of the photoproducts was rather poor. At an earlier stage of irradiation, 2-(2,2-diarylethenyl)-3-methoxy-1,4-naphthoquinone (**4**) can be

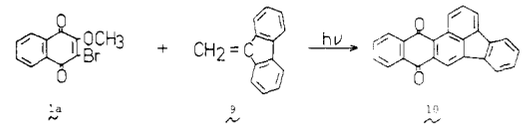


isolated.[4] **4** was found to be an intermediate and could be converted to **3** photochemically in an almost quantitative yield. The presence of pyridine in an amount equimolar to that of **1a** seemed to prevent the formation

Scheme II



Scheme III



of resinous byproducts, probably because it reacted with hydrogen bromide liberated during the course of the reaction. Hydrogen bromide might possibly cause demethylation of the methoxy group of **4**, thus forming 2-(2,2-diarylethenyl)-3-hydroxy-1,4-naphthoquinone which fails to produce the desired polycyclic aromatic quinones.

The formation of **4** suggests that the products in this photocycloaddition are determined exclusively by the nature of the leaving groups in the 2- and 3-positions of the 1,4-naphthoquinones. Thus, it may be possible to control the regioselectivity of the condensation by choosing a suitable pair of substituted 2-halogeno-1,4-naphthoquinones[5] and 1,1-diarylethylenes.

When naphthylethylenes **5** were submitted to the photochemical reaction instead of **2**, benzo[*b*]chrysene-7,12-diones **7** and/or dibenzo[*b*,*d*]phenanthrene-9,14-diones **8** were obtained similarly (Scheme II).

From the photocycloaddition reaction of **1a** with 9-methylenefluorene (**9**), naphtho[2,3-*b*]fluoranthene-9,14-dione (**10**) was isolated in 10% yield (Scheme III).

Although yields still remain to be improved, 1-alkyl-1-arylethylenes such as α-methylstyrene or 1-cyclohexylstyrene gave benz[*a*]anthracene-7,12-dione derivative **11** or **12** on reaction with **1a**. However, neither the 1,1-di-

alkylethylene nor styrene itself underwent a photocycloaddition reaction with **1a**. These results suggest that in the initial stages of the reaction charge-transfer-type π–π interaction between 2-bromo-3-methoxy-1,4-naphthoquinone and 1,1-diarylethylenes may somehow play an important role.[6]

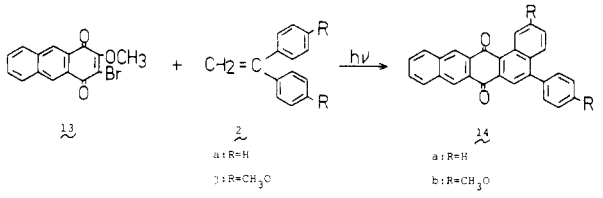
(3) (a) J. E. Tomaszewski, W. B. Manning, and G. M. Mushik, *Tetrahedron Lett.*, 971 (1977); (b) W. B. Manning, J. E. Tomaszewski, G. M. Mushik, and R. I. Sato, *J. Org. Chem.*, **42**, 3465 (1977); (c) W. B. Manning, *Tetrahedron Lett.*, 1661 (1979); (d) W. B. Manning, G. M. Mushik, and J. E. Tomaszewski, *J. Org. Chem.*, **44**, 699 (1979); (e) G. M. Mushik, J. E. Tomaszewski, R. I. Sato, and W. B. Manning, *ibid.*, **44**, 2150 (1979).

(4) The yield of this type of intermediate is dependent upon irradiation time.

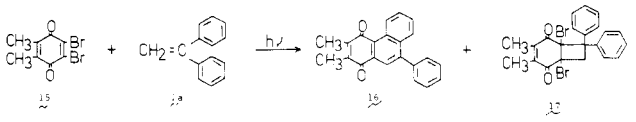
(5) Synthesis of 2,5-, 2,6-, 2,7-, and 2,8-dimethoxy-1,4-naphthoquinones was reported elsewhere [cf.: R. H. Thomson, *J. Org. Chem.*, **13**, 870 (1948); J. M. Lyons and R. H. Thomson, *J. Chem. Soc.*, 2910 (1953)]. Bromination of these quinones affords 2-bromo-3,5-dimethoxy-, 2-bromo-3,6-dimethoxy-, 2-bromo-3,7-dimethoxy-, and 2-bromo-3,8-dimethoxy-1,4-naphthoquinones which serve as starting materials for this photocyclization reaction.

(6) The cyclobutane-type cycloaddition product was isolated from the photochemical reaction of 2-methoxy-1,4-naphthoquinone with 1,1-diarylethylene. Although the cycloaddition product was rather labile against further irradiation and/or heat, resulting in the reversible formation of the starting materials, the existence of π–π interaction between one aryl group of the ethylene moiety and the quinone ring in the cycloaddition product was confirmed by NMR. Similar interactions in the initial stages of the photochemical reaction described in this work may affect the course of the subsequent cyclization reaction. Cf. T. Otsuki, *Bull. Chem. Soc. Jpn.*, **49**, 2596 (1976).

Scheme IV



Scheme V



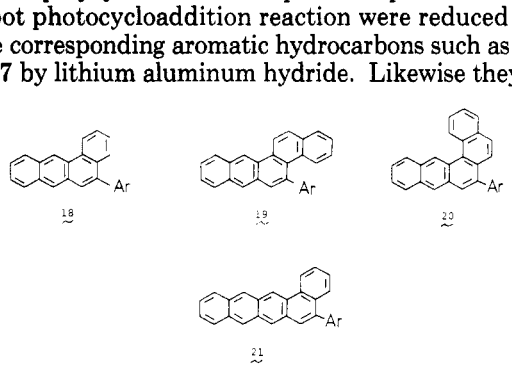
Unsymmetrical 1,1-diarylethylenes gave mixtures of polycyclic isomers as the result of the two possible cyclization modes (Scheme I).[1b] Though elucidation of factors governing the direction of cyclization is still incomplete, cyclization of an electron-donating aryl group to form a polycyclic aromatic ring appears to be more favorable. This result again suggests that π–π interaction between the starting quinone and 1,1-diarylethylene, especially one aryl group of the ethylene, in the initial stages of the reaction may control the subsequent course of the photocycloaddition reaction.

For the one-pot photocycloaddition reaction, 2,3-dihalogeno-1,4-naphthoquinones such as 2,3-dichloro-1,4-naphthoquinone (**1b**) and 2,3-dibromo-1,4-naphthoquinone (**1c**) can serve as starting materials as well as **1a**. The crucial requisites for our photocycloaddition reaction are (i) that the *p*-quinone should have good leaving groups in both the 2- and 3-positions and (ii) that other substituents on both the quinone and the 1,1-diarylethylene must not disturb the π–π interaction between quinone and ethylene in the initial stages of the reaction.

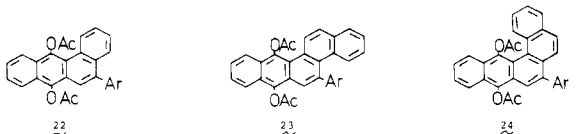
An analogous photocycloaddition using 2-bromo-3-methoxy-1,4-anthraquinone (**13**) and 1,1-diarylethylene (**2**) results in the formation of benz[*a*]naphthacene-7,14-dione (**14**, Scheme IV).

On irradiation of *p*-benzoquinone derivative **15** with **2a**, phenanthrene-1,4-dione **16** was found, accompanied by a cyclobutane-type addition product **17** (Scheme V).

These polycyclic aromatic quinones produced by the one-pot photocycloaddition reaction were reduced easily to the corresponding aromatic hydrocarbons such as **18**–**21** and **27** by lithium aluminum hydride. Likewise they were

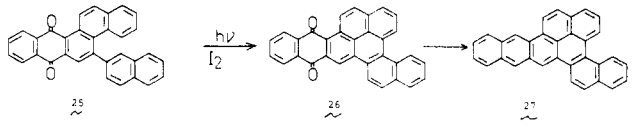


converted to the diacetoxy derivatives **22**–**24** by reductive acetylation with zinc–acetic anhydride.



When a polycyclic aromatic quinone has a favorable spatial arrangement for further intramolecular cyclization,

Scheme VI



e.g., 5-(2-naphthyl)benzo[*b*]chrysene-9,14-dione (**25**), it can be converted to another higher polycyclic aromatic compound, **26**, photochemically in the presence of iodine. Similarly, dinaphtho[1,2-*c*:2,3-*e*]pyrene (**27**) was obtained by reduction of **26** (Scheme VI).

Experimental Section

Starting Materials. 2-Bromo-3-methoxy-1,4-naphthoquinone and 2,3-dibromo-1,4-naphthoquinone were synthesized according to the literature.[7,8] 2,3-Dichloro-1,4-naphthoquinone is commercially available and was used without further purification. 2-Bromo-3-methoxy-1,4-anthraquinone was synthesized by epoxidation of 1,4-anthraquinone[9] with sodium hypochlorite, hydrolysis with sulfuric acid, etheration, and subsequent bromination with molecular bromine.[10] 2,3-Dibromo-5,6-dimethyl-*p*-benzoquinone was synthesized by bromination of 2,3-dimethyl-*p*-benzoquinone with molecular bromine.[11] 1,1-Diarylethylenes were commercially available and were used after purification by distillation or recrystallization.

Physical Properties of the Starting Materials. 2-Bromo-3-methoxy-1,4-anthraquinone (13): yellow needles; mp 176.0–180.0 °C; NMR ($CDCl_3$) δ 4.33 (3 H, s), 7.5–8.1 (4 H, m), 8.50 (1 H, s), 8.53 (1 H, s); IR (KBr) 1665 cm^{-1}; MS *m/e* 318 (M^+), 316 (M^+).

2,3-Dibromo-5,6-dimethyl-*p*-benzoquinone (15): yellow crystals; NMR ($CDCl_3$) δ 2.08 (6 H, s); IR (KBr) 1660 cm^{-1}; MS *m/e* 296 (M^+), 294 (M^+), 292 (M^+).

Photochemical Reaction. A benzene solution (25 mL) of a quinone (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 arc lamp (300 W). The amount of quinone consumed was followed by thin-layer chromatography. After the complete consumption of quinone (5–12 h), the reaction mixture was concentrated in vacuo and further purified by column chromatography on silica gel.

Physical Properties of the Products.[12] **2-(2,2-Diphenylethenyl)-3-methoxy-1,4-naphthoquinone (4)**: reddish orange needles; mp 143.0–145.0 °C; the yield is dependent upon the time of irradiation; NMR ($CDCl_3$) δ 3.77 (3 H, s), 6.66 (1 H, s), 7.3 (5 H, br s), 7.4 (5 H, br s), 7.5–8.2 (4 H, m); IR (KBr) 1640 cm^{-1}; MS *m/e* 366 (M^+).

3-Methyl-5-phenylbenz[*a*]anthracene-7,12-dione (3Af) and 5-*m*-tolylbenz[*a*]anthracene-7,12-dione (3Bf): yellow crystals; mp 163.0–166.0 °C as a mixture of two isomers; yield 47% (47/53 **3Af**/**3Bf**); NMR ($CDCl_3$) δ 2.29 (3 H, **3Af**, s), 2.43 (3 H, **3Bf**, s), 6.8–8.3 (12 H, m), 9.51 (1 H, **3Af**, d, J = 9 Hz), 9.69 (1 H, **3Bf**, d, J = 8 Hz); IR (KBr) 1670 cm^{-1}. Anal. Calcd for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 86.43; H, 4.63.

5-Phenyl-3-(trifluoromethyl)benz[*a*]anthracene-7,12-dione (3Ag) and **5-[3-(trifluoromethyl)phenyl]benz[*a*]anthracene-7,12-dione (3Bg)**: yellow crystals; mp 131.0–135.0 and 170.0–175.0 °C as a mixture of two isomers; yield 31% (16/84 **3Ag**/**3Bg**); NMR ($CDCl_3$) δ 6.8–8.7 (12 H, m), 9.61 (1 H, **3Bg**, d, J = 8 Hz), 9.75 (1 H, **3Ag**, d, J = 9 Hz); IR (KBr) 1660, 1670 cm^{-1}; UV ($CHCl_3$) 409 nm (ϵ 4.2 × 10^3), 363 (sh, 3.2 × 10^3), 334 (4.1 × 10^4), 288 (4.4 × 10^4), 255 (sh, 2.7 × 10^4), 249 (2.9 × 10^4); MS *m/e* 402 (M^+). Anal. Calcd for $C_{25}H_{13}O_2F_3$: C, 74.62; H, 3.26; F, 14.17. Found: C, 74.35; H, 3.09; F, 13.89.

(7) L. F. Fieser and R. H. Brown, *J. Am. Chem. Soc.*, **71**, 3609 (1949).
(8) T. Zincke and M. Schmidt, *Chem. Ber.*, **27**, 2758 (1894).
(9) L. F. Fieser, "Organic Experiments", D. C. Heath, Boston, MA, 1968, p 247.
(10) Cf. ref 7.
(11) Cf. ref 8.
(12) The physical properties of the photocycloaddition products not described in this text were given in ref 1b.

4-Methyl-5-phenylbenz[*a*]anthracene-7,12-dione (3Ah) and 5-*o*-tolylbenz[*a*]anthracene-7,12-dione (3Bh): yellow needles; mp 133.0–135.0 and 165.0–170.0 °C as a mixture of two isomers; yield 39% (28/72 **3Ah**/**3Bh**); NMR ($CDCl_3$) δ 2.00 (3 H, **3Ah**, s), 2.07 (3 H, **3Bh**, s), 6.9–8.3 (12 H, m), 9.50 (1 H, **3Bh**, d, J = 9 Hz), 9.69 (1 H, **3Ah**, d, J = 9 Hz); IR (KBr) 1660, 1670 cm^{-1}. Anal. Calcd for $C_{25}H_{16}O_2$: C, 86.18; H, 4.63. Found: C, 85.92; H, 4.55.

2-Methoxy-5-(4-methoxyphenyl)benz[*a*]anthracene-7,12-dione (3Ai = 3Bi): yellowish orange needles; mp 216.0–218.0 °C; yield 26%; NMR ($CDCl_3$) δ 3.96 (3 H, s), 4.08 (3 H, s), 6.9–8.5 (10 H, m), 8.22 (1 H, s), 9.41 (1 H, d, J = 3 Hz); IR (KBr) 1670 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.49; H, 4.50.

3-Methyl-5-*m*-tolylbenz[*a*]anthracene-7,12-dione (3Aj = 3Bj): yellow crystals; mp 198.0–199.0 °C; yield 73%; NMR ($CDCl_3$) δ 2.40 (3 H, s), 2.46 (3 H, s), 6.6–8.4 (10 H, m), 8.20 (1 H, s), 9.59 (1 H, d, J = 9 Hz); IR (KBr) 1660 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 85.95; H, 4.99.

4-Methyl-5-*o*-tolylbenz[*a*]anthracene-7,12-dione (3Ak = 3Bk): yellow crystals; mp 174.0–177.5 °C; yield 16%; NMR ($CDCl_3$) δ 2.00 (6 H, s), 6.8–8.4 (10 H, m), 8.13 (1 H, s), 9.62 (1 H, d, J = 8 Hz); IR (KBr) 1675 cm^{-1}. Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 85.90; H, 5.01.

1,2,3-Trimethyl-5-phenylbenz[*a*]anthracene-7,12-dione (3Al): yellow crystals; mp 207.0–208.0 °C; yield 34%; NMR ($CDCl_3$) δ 2.37 (3 H, s), 2.40 (6 H, s), 7.4 (5 H, br s), 7.2–8.2 (5 H, m), 7.96 (1 H, s); IR (KBr) 1665 cm^{-1}; UV ($CHCl_3$) 447 nm (ε 3.0 × 10^3), 442 (sh, 3.3 × 10^3), 386 (3.9 × 10^3), 257 (3.0 × 10^4), 242 (3.0 × 10^4); MS m/e 376 (M^+). Anal. Calcd for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36. Found: C, 85.51; H, 5.38.

5-(3,4,5-Trimethylphenyl)benz[*a*]anthracene-7,12-dione (3Bl): yellow crystals; mp 306.0–307.0 °C; yield 24%; NMR ($CDCl_3$) δ 2.27 (3 H, s), 2.36 (6 H, s), 7.07 (2 H, s), 7.3–8.4 (7 H, m), 8.18 (1 H, s), 9.63 (1 H, d, J = 9 Hz); IR (KBr) 1665 cm^{-1}; UV ($CHCl_3$) 445 (ε 4.3 × 10^3), 426 (4.9 × 10^3), 365 (sh, 3.2 × 10^3), 335 (5.2 × 10^4), 293 (3.8 × 10^4), 249 (3.2 × 10^4); MS m/e 376 (M^+). Anal. Calcd for $C_{27}H_{20}O_2$: C, 86.14; H, 5.36. Found: C, 85.66; H, 5.36.

5-(1-Naphthyl)benz[*a*]anthracene-7,12-dione (6a) and 5-phenylbenzo[*b*]chrysene-7,12-dione (7a): yellow crystals; mp 227.0–231.5 °C as a mixture of two isomers; yield 32% (55/45 **6a**/**7a**); NMR ($CDCl_3$) δ 7.0–8.5 (15 H, m), 9.60 (1 H, **7a**, d, J = 10 Hz), 9.86 (1 H, **6a**, dd, J = 1, 10 Hz); IR (KBr) 1659 cm^{-1}; UV ($CHCl_3$) 419 nm (ε 5.1 × 10^3), 325 (1.9 × 10^4), 286 (3.3 × 10^4), 275 (3.1 × 10^4), 256 (3.4 × 10^4). Anal. Calcd for $C_{28}H_{16}O_2$: C, 87.48; H, 4.20. Found: C, 87.71; H, 4.15.

5-(2-Naphthyl)benz[*a*]anthracene-7,12-dione (6b): yellow plates; mp 213.0–213.5 °C; yield 32%; NMR ($CDCl_3$) δ 7.4–8.5 (14 H, m), 8.45 (1 H, s), 9.85 (1 H, dd, J = 1, 9 Hz); IR (KBr) 1662 cm^{-1}; UV ($CHCl_3$) 423 nm (ε 5.9 × 10^3), 290 (4.2 × 10^4), 249 (4.3 × 10^4); MS m/e 384 (M^+). Anal. Calcd for $C_{28}H_{16}O_2$: C, 87.48; H, 4.20. Found: C, 87.69; H, 4.19.

7-Phenyldibenzo[*b*,*d*]phenanthrene-9,14-dione (8b): yellow prisms; mp 261.0–262.0 °C; yield 24%; NMR ($CDCl_3$) δ 7.4–8.6 (10 H, m), 7.6 (5 H, br s), 8.44 (1 H, s); IR (KBr) 1660 cm^{-1}; UV ($CHCl_3$) 408 nm (ε 4.8 × 10^3), 338 (3.2 × 10^4), 325 (sh, 1.9 × 10^4), 269 (4.0 × 10^4), 254 (3.9 × 10^4), 246 (4.0 × 10^4); MS m/e 384 (M^+). Anal. Calcd for $C_{28}H_{16}O_2$: C, 87.48; H, 4.20. Found: C, 87.66; H, 4.21.

5-(1-Naphthyl)benzo[*b*]chrysene-7,12-dione (7c): yellow crystals; mp 281.5–284.0 °C; yield 9%; NMR ($CDCl_3$) δ 6.7–7.2 (17 H, m), 9.76 (1 H, d, J = 9 Hz); IR (KBr) 1670 cm^{-1}; UV ($CHCl_3$) 495 nm (sh, ε 5.1 × 10^3), 445 (sh, 6.7 × 10^3), 385 (1.9 × 10^4), 348 (sh, 1.9 × 10^4), 324 (2.8 × 10^4), 277 (3.2 × 10^4), 254 (4.4 × 10^4); MS m/e 434 (M^+). Anal. Calcd for $C_{32}H_{18}O_2$: C, 88.46; H, 4.18. Found: C, 88.32; H, 4.07.

7-(2-Naphthyl)dibenzo[*b*,*d*]phenanthrene-9,14-dione (8d): yellow crystals; mp 285.5–288.5 °C; yield 47%; NMR ($CDCl_3$) δ 7.2–8.5 (17 H, m), 8.43 (1 H, s); IR (KBr) 1665 cm^{-1}; UV ($CHCl_3$) 411 nm (ε 5.9 × 10^3), 337 (2.4 × 10^4), 327 (sh, 5.4 × 10^4), 247 (5.4 × 10^4); MS m/e 434 (M^+). Anal. Calcd for $C_{32}H_{18}O_2$: C, 88.46; H, 4.18. Found: C, 88.41; H, 4.19.

5-(2-Naphthyl)benzo[*b*]chrysene-7,12-dione (7e): yellow crystals; mp 277.0–278.5 °C; yield 26%; NMR ($CDCl_3$) δ 6.9–8.5 (16 H, m), 8.50 (1 H, s), 9.64 (1 H, d, J = 9 Hz); IR (KBr) 1665 cm^{-1}; UV ($CHCl_3$) 428 nm (ε 7.2 × 10^3), 327 (3.3 × 10^4), 315 (sh, 3.0 × 10^4), 265 (5.2 × 10^4), 246 (sh, 4.4 × 10^4); MS m/e 434 (M^+). Anal. Calcd for $C_{32}H_{18}O_2$: C, 88.46; H, 4.18. Found: C, 87.59; H, 4.20.

7-(1-Naphthyl)dibenzo[*b*,*d*]phenanthrene-9,14-dione (8e). Judging from the thin-layer chromatography, **8e** was found to be produced, but its yield was too low to be identified by spectroscopic methods.

14-Methyl-5-(2-naphthyl)benzo[*b*]chrysene-7,12-dione (7*f*): orange-yellow crystals; mp 304.5–306.0 °C; yield 21%; NMR ($CDCl_3$) δ 2.84 (3 H, s), 6.3–8.5 (16 H, m), 9.41 (1 H, s); IR (KBr) 1665 cm^{-1}; MS m/e 448 (M^+). Anal. Calcd for $C_{33}H_{20}O_2$: C, 88.87; H, 4.50. Found: C, 87.04; H, 4.39.

7-(4-Methyl-1-naphthyl)dibenzo[*b*,*d*]phenanthrene-9,14-dione (8f). The formation of **8f** was suggested only by the inspection of thin-layer chromatography.

Naphtho[2,3-*b*]fluoranthene-8,13-dione (10): orange-yellow needles; mp 256.0–257.0 °C; yield 10%; NMR ($CDCl_3$) δ 7.1–8.3 (10 H, m), 8.44 (1 H, s), 9.14 (1 H, dd, J = 1, 9 Hz); IR (KBr) 1665 cm^{-1}; UV ($CHCl_3$) 418 nm (ε 5.8 × 10^3), 374 (4.8 × 10^3), 350 (sh, 4.7 × 10^3), 330 (sh, 8.9 × 10^3), 286 (4.9 × 10^4), 254 (sh, 1.9 × 10^4), 241 (2.0 × 10^4); MS m/e 332 (M^+). Anal. Calcd for $C_{24}H_{12}O_2$: C, 86.73; H, 3.64. Found: C, 85.45; H, 3.57.

5-Methylbenz[*a*]anthracene-7,12-dione (11): yellow crystals; mp 178.0–178.5 °C; yield 17%; NMR ($CDCl_3$) δ 2.79 (3 H, s), 7.4–8.4 (8 H, m), 9.69 (1 H, d, J = 8 Hz); IR (KBr) 1670 cm^{-1}; MS m/e 272 (M^+). Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.80; H, 4.44. Found: C, 83.59; H, 4.36.

5-Cyclohexylbenz[*a*]anthracene-7,12-dione (12): yellow oil; yield 5%; NMR ($CDCl_3$) δ 1.6–2.2 (11 H, m), 7.2–8.4 (8 H, m), 9.83 (1 H, d, J = 9 Hz); IR (liquid film) 1670 cm^{-1}.

5-Phenylbenzo[*a*]naphthacene-7,14-dione (14a): orange-yellow crystals; mp 269.0–270.0 °C; yield 50%; NMR ($CDCl_3$) δ 7.4–8.6 (7 H, m), 7.5 (5 H, br s), 8.40 (1 H, s), 8.76 (1 H, s), 8.82 (1 H, s), 9.85 (1 H, d, J = 10 Hz); IR (KBr) 1664 cm^{-1}; UV ($CHCl_3$) 412 nm (ε 8.9 × 10^3), 312 (4.7 × 10^4), 243 (5.1 × 10^4); MS m/e 384 (M^+). Anal. Calcd for $C_{28}H_{16}O_2$: C, 87.48; H, 4.20. Found: C, 87.72; H, 4.19.

2-Methoxy-5-(4-methoxyphenyl)benzo[*a*]naphthacene-7,14-dione (14b): orange crystals; mp 275.0–277.0 °C; yield 43%; IR (KBr) 1675 cm^{-1}; MS m/e 444 (M^+). Anal. Calcd for $C_{30}H_{20}O_4$: C, 81.06; H, 4.54. Found: C, 80.82; H, 4.78.

2,3-Dimethyl-9-phenylphenanthrene-1,4-dione (16): yellow crystals; mp 168.0–169.5 °C; yield 35%; NMR ($CDCl_3$) δ 2.16 (3 H, s), 2.22 (3 H, s), 6.8–8.3 (8 H, m), 8.10 (1 H, s), 8.53 (1 H, dd, J = 2, 8 Hz); IR (KBr) 1670 cm^{-1}; UV ($CHCl_3$) 427 nm (ε 2.0 × 10^3), 373 (2.1 × 10^3), 286 (2.4 × 10^4), 241 (1.8 × 10^4); MS m/e 312 (M^+).

1,6-Dibromo-3,4-dimethyl-7,7-diphenylbicyclo[4.2.0]oct-3-ene-2,5-dione (17): white crystals; mp 162.5–164.0 °C; yield 35%; NMR ($CDCl_3$) δ 1.78 (3 H, s), 1.88 (3 H, s), 3.48 (1 H, d, J = 8 Hz), 4.26 (1 H, d, J = 8 Hz), 6.9–7.6 (10 H, m); IR (KBr) 1675 cm^{-1}; MS m/e (relative intensity) 395 (M^+ – 79, 59), 393 (M^+ – 81, 52), 314 (M^+ – 160, 100), 180 (29).

Reduction of *p*-Quinones to the Corresponding Polycyclic Aromatic Compounds. A tetrahydrofuran solution (50 mL) of a *p*-quinone (0.05 mmol) and an excess amount (ca. 3 equiv) of lithium aluminum hydride was refluxed for 8 h. After hydrolysis of the excess amount of lithium aluminum hydride, the reaction mixture was purified by column chromatography on silica gel.

Physical Properties of Polycyclic Aromatic Compounds. 5-(2-Naphthyl)benzo[*b*]chrysene (19, Ar = 2-Naphthyl): pale yellow crystals; mp 209.0–213.0 °C; yield 74%; NMR ($CDCl_3$) δ 6.7–8.4 (17 H, m), 8.30 (1 H, s), 8.82 (1 H, d, J = 8 Hz), 9.11 (1 H, s); IR (KBr) neither CO nor OH; UV ($CHCl_3$) 400 nm (sh, ε 3.2 × 10^3), 390 (sh, 4.5 × 10^3), 373 (6.2 × 10^3), 356 (6.1 × 10^3), 3.11 (6.1 × 10^4), 297 (7.0 × 10^4), 293 (7.0 × 10^4), 260 (4.9 × 10^4), 243 (4.6 × 10^4); MS m/e 404 (M^+).

7-Phenyldibenzo[*b*,*d*]phenanthrene (20, Ar = Phenyl): pale yellow crystals; mp 207.0–208.5 °C; yield 77%; NMR ($CDCl_3$) δ 6.9–8.2 (15 H, m), 8.32 (1 H, s), 9.13 (1 H, d, J = 8 Hz), 9.43 (1 H, s); IR (KBr) neither CO nor OH; UV (C_2H_5OH) 312 nm (ε 7.3 × 10^4), 300 (5.8 × 10^4), 288 (3.5 × 10^4), 250 (5.1 × 10^4), 227

(7.7×10^4), 204 (9.3×10^4); UV (C_6H_6) 398 nm (ϵ 3.7×10^3), 378 (5.7×10^3), 361 (5.4×10^3), 344 (4.1×10^3). Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 95.04; H, 5.07.

5-Phenylbenzo[*a*]naphthacene (21, Ar = Phenyl): pale yellow crystals; mp 160.0–165.0 °C; yield 33%; NMR ($CDCl_3$) δ 6.6–8.4 (14 H, m), 8.45 (1 H, s), 8.58 (1 H, s), 8.69 (1 H, s), 8.85 (1 H, d, J = 8 Hz); MS m/e 354 (M^+). Anal. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 94.35; H, 5.01.

Dinaphtho[1,2-*c*:2,3-*e*]pyrene (27): yellow crystals; mp 298.0–300.5 °C; yield 58%; IR (KBr) neither CO nor OH; UV (C_6H_6) 462 nm (ϵ 2.4×10^4), 434 (2.0×10^4), 410 (1.0×10^4), 388 (4.5×10^3), 366 (sh, 3.8×10^3), 338 (sh, 6.5×10^4), 329 (1.1×10^5), 317 (8.6×10^4), 294 (3.9×10^4), 281 (4.7×10^4); MS m/e 402 (M^+). Anal. Calcd for $C_{32}H_{18}$: C, 95.49; H, 4.51. Found: C, 95.02; H, 4.39.

Reductive Acetylation of *p*-Quinones. *p*-Quinone (0.1 mmol) and an excess amount of zinc powder were added to acetic anhydride (10 mL). Then the reaction mixture was refluxed for 30 min. After the yellow color of the solution due to the *p*-quinone disappeared completely, the reaction mixture was hydrolyzed and neutralized with sodium acetate. The diacetate was extracted with ether from the reaction mixture and purified further by column chromatography on silica gel.

Physical Properties of Diacetates. 7,12-Diacetoxy-5-(2-naphthyl)benzo[*b*]chrysene (23, Ar = 2-Naphthyl): pale yellow crystals; mp 289.0–290.0 °C; yield 64%; NMR ($CDCl_3$) δ 2.54 (3 H, s), 2.58 (3 H, s), 6.6–8.3 (17 H, m), 9.11 (1 H, d, J = 10 Hz); IR (KBr) 1765 cm^{-1}; UV ($CHCl_3$) 415 nm (ϵ 7.8×10^3), 392 (1.1×10^4), 372 (8.4×10^3), 352 (5.9×10^3), 314 (7.7×10^4), 301 (8.7×10^4), 259 (5.0×10^4), 248 (5.2×10^4); MS m/e (relative intensity) 520 (M^+, 29), 478 (41), 436 (100). Anal. Calcd for $C_{36}H_{24}O_4$: C, 83.06; H, 4.56. Found: C, 83.04; H, 4.50.

9,14-Diacetoxy-7-phenyldibenzo[*b*,*d*]phenanthrene (24, Ar = Phenyl): pale yellow crystals; yield 78%; NMR ($CDCl_3$) δ 1.60 (3 H, s), 2.62 (3 H, s), 7.6 (5 H, br s), 7.2–8.4 (11 H, m); IR (KBr) 1765 cm^{-1}; MS m/e 470 (M^+).

Photochemical Cyclization Reaction of a *p*-Quinone to the Higher Homologue. On irradiation of a benzene solution (400 mL) of **25** (0.15 mmol) and iodine (0.6 mmol) with a high-pressure Hg arc lamp for 30 h, the starting *p*-quinone (**25**) was consumed completely. The reaction mixture was washed with an aqueous solution of sodium bisulfite to eliminate iodine, and the organic layer was dried over sodium sulfate. Concentration of the reaction mixture gave red crystals of **dinaphtho[1,2-*c*:2,3-*e*]pyrene-11,16-dione (26)**: mp 284.0–286.0 °C; yield 85%; IR (KBr) 1670 cm^{-1}; UV ($CHCl_3$) 494 nm (ϵ 1.1×10^4), 380 (sh, 1.2×10^4), 349 (2.8×10^4), 335 (2.8×10^4), 304 (6.1×10^4), 282 (3.9×10^4), 250 (sh, 4.3×10^4), 245 (4.5×10^4); MS m/e 432 (M^+). Anal. Calcd for $C_{32}H_{16}O_2$: C, 88.82; H, 3.73. Found: C, 88.03; H, 3.85.

Registry No. **1a**, 26037-61-6; **2a**, 530-48-3; **2f**, 4333-70-4; **2g**, 395-10-8; **2h**, 947-77-3; **2i**, 4356-69-8; **2j**, 10605-48-8; **2k**, 2919-19-9; **2l**, 72853-68-0; **3Af**, 72853-69-1; **3Bf**, 72853-70-4; **3Ag**, 72853-71-5; **3Bg**, 72853-72-6; **3Ah**, 72853-73-7; **3Bh**, 72853-74-8; **3Ai**, 72735-91-2; **3Aj**, 72853-75-9; **3Ak**, 72853-76-0; **3Al**, 72853-77-1; **3Bl**, 72853-78-2; **4**, 72853-79-3; **5a**, 28358-65-8; **5b**, 28358-66-9; **5c**, 39666-29-0; **5d**, 39799-27-4; **5e**, 67132-22-3; **5f**, 67132-23-4; **6a**, 72853-50-0; **6b**, 72853-51-1; **7a**, 67132-24-5; **7c**, 67132-25-6; **7e**, 67132-26-7; **7f**, 67132-27-8; **8b**, 72853-52-2; **8d**, 72853-53-3; **8e**, 72853-54-4; **8f**, 72853-55-5; **9**, 4425-82-5; **10**, 72853-56-6; **11**, 58024-08-1; **12**, 54988-91-9; **13**, 72853-57-7; **14a**, 72853-58-8; **14b**, 72853-59-9; **15**, 38969-08-3; **16**, 72853-60-2; **17**, 72853-61-3; **19**, 67132-28-9; **20**, 72853-62-4; **21**, 72853-63-5; **23**, 72853-64-6; **24**, 72853-65-7; **25**, 67132-26-7; **26**, 72853-66-8; **27**, 72853-67-9.

Microbial Stereodifferentiating Reduction of (±)-4-Methyl- and (±)-6-Methyl-1-oxo[2.2]metacyclophanes and Revision of the Absolute Configuration of 4-Substituted [2.2]Metacyclophanes

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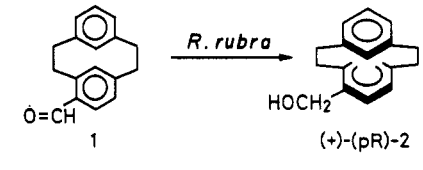
Partial oxidative hydrolysis of 4-bromo-1,1,10,10-bis(trimethylenedithio)[2.2]metacyclophane (**7**) yielded the bromo ketones **8** and **9** which were respectively converted into (±)-4-methyl- (**3**) and (±)-6-methyl-1-oxo[2.2]-metacyclophanes (**4**). The unambiguous synthesis of (±)-**3** from 2,5-dimethylbenzoic acid (**18**) assigned their structures. Incubation of (±)-**3** with *Rhodotorula rubra* gave a mixture of (−)-ketone **3**, (−) axial alcohol **38**, and (−) equatorial alcohol **39**. The observed (−) Cotton effect indicated the *pS* configuration of (−)-**3**, and transformation of (−)-**3** into (+)-4-methyl[2.2]metacyclophane (**5**) permitted the assignment of the *pR* configuration to (+)-**5**, opposite to Schlögl's proposal. This conclusion was further supported by the parallel sequence of steps starting from (±)-6-methyl ketone **4**.

In our preceding paper[1] which described our exploration of the application of the proposed "quadrant rule"[2] in [2.2]metacyclophane derivatives, we reported isolation of 4-hydroxymethyl[2.2]metacyclophane (**2**) (optical purity 11.7%) enriched in the (+)-(*pR*)-enantiomer from a culture solution of *Rhodotorula rubra* containing (±)-[2.2]metacyclophane-4-carboxaldehyde (**1**). (See Chart I.)

If a favorable conformation of the substrate **1** is assumed, the quadrant rule suggests the *pR* configuration for the (+)-hydroxymethyl derivative **2**, which is opposite to Schlögl's proposal[3] based on the "kinetic resolution" method. This discrepancy prompted us to reinvestigate the absolute configuration of 4-substituted [2.2]metacyclophanes.

Chart I



1 (+)-(pR)-2

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