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Reactions of 5,6-Dilithioacenaphthene-*N*,*N*,*N'*,*N'*-Tetramethyl-1,2-ethanediamine Complex with *α*-Diketones. II.[1] Competitive Oxophilic and Carbophilic Additions and Redox Reactions

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(Received January 8, 1981)

The reaction of the title complex (**3**) with benzil did not give the 1 : 1 cyclic addition product expected, but gave 5,6-dibenzoylacenaphthene, 5-(1-hydroxy-2-oxo-1,2-diphenylethyl)-6-(2-oxo-1,2-diphenylethoxy)acenaphthene (**5**), 5-benzoyl-6-(1-hydroxy-2-oxo-1,2-diphenylethyl)acenaphthene, benzoin, and benzilic acid. Compound **5** suggests a new type of oxophilic addition accompanied by a carbophilic addition. The reaction of **3** with 9,10-phenanthrenequinone in a 1 : 1 molar ratio gave both the oxidative homo-coupling product of **3**, 1,2,7,8-tetrahydrodicyclopenta[*cd* : *lm*]perylene, and the hydroquinone dianion, which was converted into 9,10-diacetoxyphenanthrene on acetolysis. The differences in the reaction modes between **3** and α-diketones can basically be understood in terms of the redox potentials and the steric factors of the α-diketones.

5,6-Dilithioacenaphthene (**1**)[2,3] can be regarded as a nucleophile like 1,8-dilithionaphthalene (**2**)[4–8] which possesses two reaction sites at the peri positions of a naphthalene nucleus; thus, its synthetic conditions and reaction modes especially with bifunctional electrophiles are of interest in connection with the peri interaction in naphthalene derivatives.[9] A 1 : 1 cyclic condensation or addition is the most possible reaction path in the reaction systems of **1** and **2** with 1,2-dichlorodisilanes,[2,8] 1,3-dichlorodisiloxanes,[2] or acenaphthenequinone (ACQ),[3,5] **1** with pyracenequinone (5,6-dihydrocyclopent[*fg*]acenaphthylene-1,2-dione; PYQ),[3] and **2** with dialkyldichlorosilanes[6] or organotin dihalides.[7] No other reaction mode except a 2 : 2 cyclic condensation in the last case[7] has been reported.

In the course of studies on the synthetic conditions of **1**, the authors have found that the 5,6-dilithioacenaphthene-*N*, *N*, *N'*, *N'*-tetramethyl-1,2-ethanediamine (TMEDA) complex (**3**)[1] reacts with some α-diketones in unexpected, novel modes which may illustrate new aspects of the peri interaction. This paper is chiefly concerned with the complicated reactions of **3** with benzil (Bz_2) and the redox reaction between **3** and 9,10-phenanthrenequinone (PQ). The factors that govern the reaction modes will also be discussed.

Results and Discussion

*Competitive Complex Reactions of **3** with Benzil; Oxophilic Addition, Carbophilic Additions, and Reduction of Benzil.* The *cis*-directing 1 : 1 cyclic additions of **3** with ACQ, PYQ, and biacetyl (Ac_2), reported separately,[1] prompted us to examine the reaction with benzil. The product expected, *cis*- or *trans*-1,2,5,6-tetrahydro-1,2-diphenylcyclopent[*fg*]acenaphthylene-1,2-diol (**4**), however, was not detected in the reaction mixture. Five products were isolated and identified as follows: 5-(1-hydroxy-2-oxo-1,2-diphenylethyl)-6-(2-oxo-1,2-diphenylethoxy)acenaphthene (**5**), 5-benzoyl-6-(1-hydroxy-2-oxo-1,2-diphenylethyl)acenaphthene (**6**), 5,6-dibenzoylacenaphthene (**7**), benzoin (**8**), and benzilic acid (**9**). Typical yields are cited in Table 1. The structure of **5** was determined by means of a single-crystal X-ray analysis. The details of this analysis are reported elsewhere.[10] Figure 1 shows one of the two crystallographically independent molecules of **5**. Probably because of packing forces, their geometries are slightly different.[10]

The ^{1}H NMR spectrum of **5** shows some unusual features, one of which is that the signal assigned to the methine proton of the *O*-substituted benzoin moiety

Table 1. Reactions of 5,6-dilithioacenaphthene–TMEDA complex (**3**) with α-diketones (in Et_2O)

α-Diketone	Mole ratio (diketone/**3**)	Reaction time/h[a]				Consumption of **3**/%[b]	Recovery of diketone/%	Product	Yield/%[c]		Mp/°C[d]
		i	ii	iii	iv				A	B	
Bz_2	2.0	0.5	2	0.5	1	100	3.7	**5**	7.9		181.0—182.5
								6	4.1		201.0—204.0 (dec/Ar)
								7[e]	21		209.0—210.0
								8[f]		19	135.0—136.0
								9[f]		4.3	151.0—152.0
PQ	1.0	0.1	1	1	0	76	62	**10**	20		345.0—346.0 (dec/Ar)
	2.1	0.1	1	1	0	98	69	**10**	27		
	1.0	0.1	4	2+1[g]	0	87	0	**10**	27		
								11[h]		48	203.0—204.0

a) Step i: Adding of diketone to **3** at −10—0 °C; Step ii: Stirring at −10—0 °C; Step iii; Stirring without cooling; Step iv: Refluxing. b) Based on GLC-peak-area of acenaphthene in hydrolyzed sample. c) A: Based on 5,6-dibromoacenaphthene; B: Based on α-diketone used. d) Some melting points were measured in argon-filled, sealed capillaries. e) Lit,[11] mp 207—208 °C. f) An authentic sample was obtained commercially. g) Treatment with Ac_2O/pyridine. h) Lit,[12] mp 203—203.5 °C.

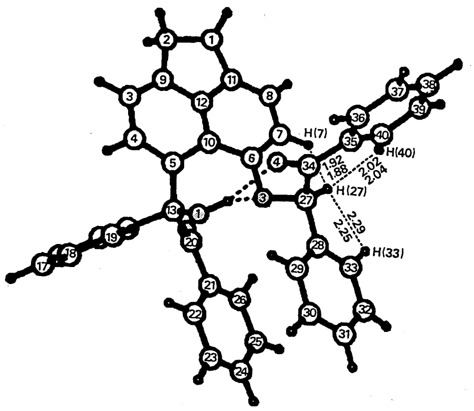


Fig. 1. Molecular structure of **5**. Some close H–H contacts (Å) are also shown, e.s.d.'s being 0.06—0.08 Å.

appears as a doublet (J=7.5 Hz) at δ 6.45 coupling with an aromatic proton, the signal of which appears as a multiplet at 7.00 (in $(CD_3)_2SO$).[13] This remarkably large long-range coupling-constant must ascribed to the specific conformation of **5** in which the methine H-atom, H(27), is in contact with three aromatic H-atoms: H(7), H(33), and H(40) (Fig. 1).[10,14]

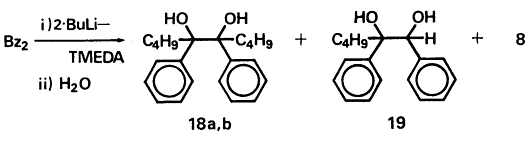
The structure of **5** suggests a new type of oxophilic addition which cooperates with a normal carbophilic addition. This is the first example of the heterophilic addition of an organolithium compound with an α-diketone; in the case of Grignard reagent, not a few instances of this type of reactions have been reported.[15] These heterophilic additions have shown the radical character of some Grignard reactions with certain carbonyl compounds.[16] As discussed below, products **5** and **8** also suggest strongly that the radical processes that involve the benzil radical anion ($Bz_2^{-\cdot}$) take an important part in the reaction with **3**.

According to the reports published on the reduction of benzil,[17—21] $Bz_2^{-\cdot}$ generated *via* a single-electron-transfer (SET) in the presence of metal cation forms an ion pair, $Bz_2^{-\cdot}Li^+$ (≡**12a**⇌*cis*-**12b**⇌*trans*-**12b**), and disproportionates to benzil and dilithium stilbenediolate (**13**) which is converted into **8** on hydrolysis (Scheme 1, path A). The formation of **5** can most readily be accounted for when the redox reaction of benzil with a probable intermediate (**14**) is assumed: The SET between the two followed by the coupling of the resulting radicals, **15** and **12b**, will yield stilbene derivative **16**, which can be converted into **5** on hydrolysis[22] (Scheme 1, path B). The other coupling product (**17**), sterically unfavorable, was not detected in the reaction mixture.

Although **7** is the major product, no positive evidence that elucidates a mechanism for its formation has been obtained. However, a by-product expected for the oxidative fission of **17** (R=H), benzoic acid, was not detected in the reaction mixture. There is a possibility that 1 : 1 cyclic addition product **4** is formed but decomposes to yield **7**. This seems to be excluded because of the stabilities of *trans*-**4**,[11] *cis*-diaryl-1,2-acenaphthenediols,[23] and the methyl analogues, *cis*- and *trans*-1,2,5,6-tetrahydro-1,2-dimethylcyclopent[*fg*]-acenaphthylene-1,2-diols,[1] though the exact factor that prevents the formation of **4** is not yet clear.

An acidification of the aqueous layer after hydrolysis gave benzilic acid. On treatment of benzil in an ethereal solution with an aqueous lithium hydroxide in the presence of TMEDA, benzilic acid rearrangement[24] did not take place. Hence, the acid must be formed in the reaction system before hydrolysis.[25]

In order to evaluate the reducing potential of the butyllithium (n-BuLi)–TMEDA complex, it was allowed to react with benzil in a molar ratio of n-BuLi : Bz_2= 2 : 1 under the conditions similar to those in the case



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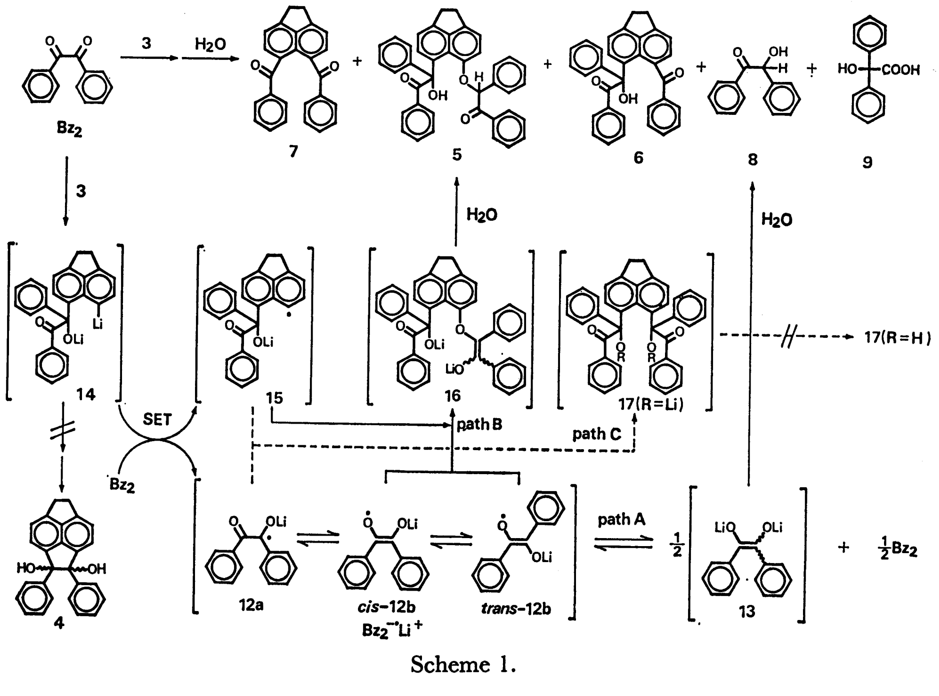
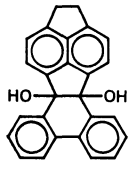


Scheme 1.

of **3** with Bz_2. From the reaction mixture, *erythro*- or *threo*-5,6-diphenyl-5,6-decanediol (46% of **18a** and 22% of 1 : 4 mixture of **18a** and **18b**),[26] 5% of 1,2-diphenyl-1,2-hexanediol (**19**), and 2% of benzoin were isolated (Eq. 1). Thus, the reducing effect of an excess *n*-BuLi which may remain in the solution of **3**[27] is negligible.

Oxidative Homo-coupling of 3. Although the reactions of *o*-quinones ACQ and PYQ with **3** yield 1 : 1 cyclic addition products,[1] another *o*-quinone, 9,10-phenanthrenequinone (PQ), has not yielded such a product (**20**). The reaction of **3** with PQ in a 1 : 1 molar ratio gave both the oxidative homo-coupling product of **3**, 1,2,7,8-tetrahydrodicyclopenta[*cd* : *lm*]-perylene (**10**; 27%), and the hydroquinone dianion (PQ^{2-}), which was converted into 9,10-diacetoxyphenanthrene (**11**; 48%) on acetolysis, as described below in detail. Thus, the redox reaction between **3** and PQ took place preferentially. This is a novel instance of the behavior of a bifunctional organolithium compound in the system with quinones, although the homo-coupling of monofunctional Grignard reagent or organolithium compound is often induced by certain quinones.[28] In the case of PQ, however, many normal additions with such organometals[29] and some oxophilic additions with aryl and allyl Grignard reagents[15] have been reported, but homo-coupling products are described only in the cases of *p*-tolyl-[29c] and *p*-methylbenzyl-[29d] magnesium bromides.



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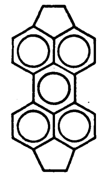

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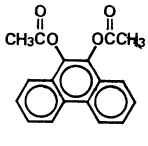

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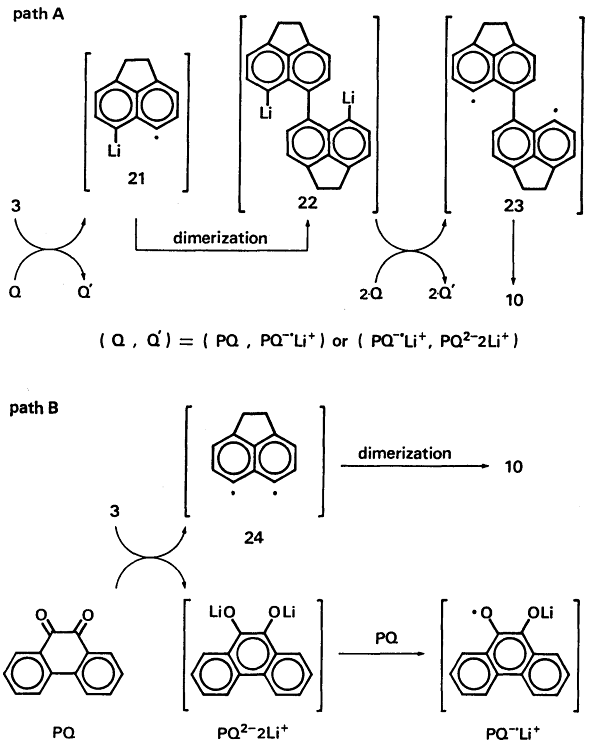
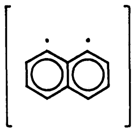
The molar ratio of PQ to **3** dramatically changed the appearance of the reaction. When an equivalent mol of PQ was added to a pale red solution of **3** over a period of 5 min, every portion of the yellow powder of PQ rapidly dissolved, the solution developed instantaneously a brilliant green color; just after the adding had been ended, the consumption-ratio of **3** was 50—60% and the reaction mixture became a dark green suspension involving a dark yellow powder of **10**. When the reaction was allowed to continue, the consumption-ratio increased and finaly reached to *ca.* 90%, and the suspension gradually changed to yellow. After a treatment with an aqueous iron(III) chloride, 60—70% of PQ was recovered, while a treatment with acetic anhydride gave a *ca.* 50% yield of 9,10-diacetoxyphenanthrene and no PQ. When a 2 molar ratio of PQ was used, the consumption of **3** was approximately quantitative just after the adding and the dark green suspension which resulted did not change its color for at least 2 h. The maximum yield of **10** was 27% regardless of the molar ratio, but in the case of that of 1 : 1, the yield depended on the reaction-time (Table 1).

The reduction of PQ and the behavior of its radical anion ($PQ^{-\cdot}$) and dianion (PQ^{2-}) in the presence of metal cation have been well documented.[15a,30—32] On the bases of these reports, the observations described



Scheme 2.



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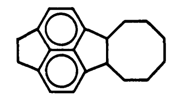

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above strongly suggest that a SET between PQ or $PQ^{-}\cdot Li^{+}$ and **3** or **22** (Scheme 2, path A) is more operative than a single two-electron-transfer between PQ and **3**, followed both by the homo-coupling of the resulting biradical (**24**) and by the redox reaction between PQ^{2-} and PQ[31] (Scheme 2, path B). This idea was further examined.

By reference to the trapping experiments of 1,8-dehydronaphthalene (**25**),[33] the reaction of **3** with PQ was investigated in the presence of a 77 molar ratio of cyclooctene,[34] but the yield of **10** was not decreased (26%) and no cyclooctene adduct (**26**) was detected. This may disprove the presence of the *free* biradical (**24**).[35]

The oxidative homo-coupling reactions of aromatic dilithium compounds by transition metal halides have been reported in the cases of **2**,[33] *o*-dilithiobenzene,[36] and 2,2'-dilithiobiphenyl,[37] and no evidence for the corresponding biradicals has been obtained. For comparison, the reaction of **3** with a 2 molar ratio of cobalt(II) chloride was investigated: complex **3** was readily decomposed by $CoCl_2$ above −30 °C, the consumption-ratio reached to ≥95% within 2 h, and **10** was isolated in a 28% yield.

The similarities between the reactions with PQ and $CoCl_2$ in the reaction rate and the yield of **10** are quite in agreement with the idea that oxidative homo-coupling of **3** proceeds in a step-wise SET pathway regardless of the oxidizing agent. In fact, the reactions of **3** with

Table 2. Cyclic voltammetric data for reduction of α-diketones (in CH_3CN, [diketone]=1.3 mmol dm^{-3}, $[Et_4NClO_4]$=0 2 mol dm^{-3}, at 20 °C)

α-Diketone	Scan rate / $V\ s^{-1}$	1st wave A/V	1st wave B/mV	1st wave C	2nd wave A/V	2nd wave B/mV	2nd wave C
PQ	0.2	−1.13	60	1.0	−1.82	105	1.0
ACQ	0.14	−1.39	60	1.0	−2.15	80	1.0
PYQ	0.2	−1.52	140	1.0	−2.25	155	1.0
	0.01	−1.52	75	1.0	−2.25	85	1.0
Bz_2	0.2	−1.66	85	1.0	−2.31	155	0.7
	0.01	−1.66	50	1.0	−2.24	100	0.5
Ac_2	0.2	<−1.8	—	—	—	—	—

A: Half-wave potential *vs.* Ag/satu. $AgNO_3$. *B*: Peak-separation. *C*: Anodic-peak-current/cathodic-peak-current.

some *p*-quinones also yielded **10** (see Experimental). On the other hand, detailed examinations confirmed that other α-diketones (ACQ, PYQ, Bz_2, and Ac_2) did not induce the homo-coupling of **3**. This indicates that the redox potential of α-diketone may be an important control-factor of the reaction modes.

Redox Potentials of α-Diketones. As Table 2 shows, the one- and two-electron reductions of the α-diketones are easier in the order of

$$\mathrm{PQ} > \mathrm{ACQ} > \mathrm{PYQ} > Bz_2 > Ac_2, \qquad (2)$$

under the conditions where the ion-pairing effect[17c,32] is negligible. Then, the effects of lithium cation and TMEDA, which may prevent the ion-pairing,[38] were examined.

All the cyclic voltammograms measured in the presence of lithium perchlorate in an acetonitrile solutions[39] are complex and correspond to irreversible steps; thus, quantitative discussions are difficult. In the case of PQ, however, the clear, positive shifts of the cathodic peaks were observed. This can be explained in terms of the formation of an ion pair $PQ^{-\cdot}Li^+$, as in the literature.[32] As expected, these positive shifts were reduced by adding TMEDA, but its effect was relatively slight. In the cases of ACQ, PYQ, and Bz_2, the positive shifts were not so clear as in the case of PQ, and no distinct effect of TMEDA was observed at any scan rate (<0.27 V s^{-1}). These findings suggest that the order of the reduction potentials (Eq. 2) may be unchanged in the ethereal solution containing Li^+–TMEDA. Thus, PQ is the most reducible α-diketone in those investigated regardless of the presence of Li^+. The relatively low reducibility of benzil even under the influence of ion-pairing supports the idea that only the sterically hindered intermediate, **14**, is able to reduce benzil in the reaction system with **3**, as discussed before. On the other hand, the difference between PQ and ACQ in redox potential seems to be too small to contribute to the distinct disparity in their reaction modes toward **3**. In fact, the reactions of these *o*-quinones with monofunctional organometals proceed in almost the same modes involving normal[23,29] and unusual[40] carbophilic additions and redox reactions.[15a] It is clear that the specific structure of **3** has revealed an unknown difference between the two *o*-quinones, though its exact nature can not yet be explained.

Experimental

General Procedures. Melting points, electron spectra, fluorescence excitation- and emission-spectra, IR spectra, ^1H NMR spectra, and mass spectra were recorded according to the methods given in the previous paper.[1] The solution of **3** was prepared from 5,6-dibromoacenaphthene, *n*-BuLi, and TMEDA in dry ether at −10—0 °C just before use, as in the previous paper.[1] All other chemicals were obtained commercially.[41] Benzil[41a] and 9,10-phenanthrenequinone[41a] were recrystallized from ethanol and benzene, respectively, and ground down and degassed *in vacuo* before use. Tetraethylammonium perchlorate[41b] was dried *in vacuo* at room temperature. Lithium perchlorate[41c] was dried at 200 °C/0.1 mmHg[†] for 2 h. Acetonitrile (Dotite Spectrosol)[41b] was dried with Molecular Sieves 5A and degassed with argon-bubbling. All reactions were performed under an argon atmosphere. All evaporations were carried out under a reduced pressure on a rotary evaporator below *ca.* 40 °C. Chromatographic separations were carried out on the columns (2.2 cm×60—90 cm) of Wakogel C-200.[41b] Analytical determinations by GLC were carried out according to the previous paper.[1]

Reactions of 3 with Benzil. To a solution of **3** (10.0 mmol in 300 cm^3 of ether), a solution of benzil[42] (4.280 g, 20.36 mmol in 50 cm^3 of ether) was added with stirring over a period of 30 min at −10—0 °C. The solution became at first dark brown, changed to dark green, and finally to a brown purple suspension. This was stirred for 2 h at −10—0 °C and for 0.5 h without cooling, and then refluxed for 1 h. After the suspension was allowed to stand for 30 min, aqueous ammonium chloride (30 g/100 cm^3) was added to it with vigorous stirring. The hydrolysate was then cooled on an ice bath for 2 h. The pale yellow precipitate which formed was filtered off, washed with water and ether, and dried *in vacuo*, giving a mixture of **5** and **7**. This was chromatographed on a silica-gel column (150 g) with benzene and chloroform as successive eluents, giving 286 mg of crude **5** (mp 177—180 °C) and then 461 mg of crude **7** (mp 199—205 °C). The combined filtrate was separated and the organic layer was washed with 3×100 cm^3 of aqueous concd sodium chloride. The combined aqueous layer was acidified with concd hydrochloric acid and allowed to stand for a few days, giving 160 mg of pure benzilic acid (**9**). The acidic solution was then extracted with ether and gave additional **9** (39 mg); the total yield was 4.3%: mp and mixed mp 151.0—152.0 °C. The organic mother layer was dried ($MgSO_4$), concentrated to about 50 cm^3, and then cooled for one day at −15 °C, giving 167 mg of crude **5** (mp 174—176 °C). The filtrate was then evaporated and the residue was triturated with ether, giving 432 mg of crude **8** (mp 122—133 °C). The filtrate of this trituration was evaporated to dryness and chromatographed on a silica-gel column (150 g) with benzene as eluent. The dark brown solution became dark green on this column. The first green eluent was collected and evaporated, and the brown residue was dissolved in carbon tetrachloride. The solution was then diluted with hexane, giving 108 mg of crude **6** as a pale brown crystal (mp 194—205 °C (dec)). The second yellowish green eluent was treated as described above for the first, giving 159 mg (3.7%) of benzil. The filtrate of this treatment was evaporated to dryness and the residue was recrystallized from ethanol, giving 83 mg of crude **6** (mp 180—182 °C). After the third deep green eluent (unknown), extraction with chloro-

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[†] 1 mmHg≃133.3 Pa.

from gave the fourth pale yellow eluent. This was evaporated to dryness, giving 390 mg of crude **8** (mp 128—132 °C). The fifth dark green eluent with chloroform was evaporated to dryness and then recrystallized from benzene, giving 306 mg of crude **7** (mp 206.5—208.5 °C). The total of 822 mg (19%, based on benzil used) of crude benzoin was decolorized in a short benzene-silica-gel column and then recrystallized from ethanol,[43] giving 547 mg (12.7%) of pure **8**; mp and mixed mp 135.0—136.0 °C.

5-(1-Hydroxy-2-oxo-1,2-diphenylethyl)-6-(2-oxo-1,2-diphenylethoxy)acenaphthene (5): A total of 453 mg (7.9%) of crude product was recrystallized from benzene,[43] giving 331 mg (5.8%) of pure **5** as white plates: mp 181.0—182.5 °C; UV$_{\max}$ (C_2H_5OH) 214 (logε 4.65), 240 (4.69), 300 (3.99), 318sh (3.87), and 334sh nm (3.66); Fluorescence$_{\max}$ (C_2H_5OH) 402 nm (excitation at 341 nm); IR 3425 (OH),3065, 3035, 2920, 1670 (C=O), 1600, 1450, 1265, 1225, 1140, 965, 855, 770, 750, 720, 705, and 695 cm^{-1}; NMR δ($CDCl_3$)$=$7.83—7.73 (4H, m, ArH), 7.68—6.80 (20H, m, ArH), 6.64 (1H, d, *J*=7.5 Hz, CH), and 3.30 (4H, s, 2CH$_2$), δ(($CD_3)_2SO$)$=$7.98—7.91 (2H, m, ArH), 7.70—6.80 (22H, m, ArH), 6.45 (1H, d, *J*=7.5 Hz, CH), and 3.29 ((4H), s, 2CH$_2$); MS (270 °C, 75 eV), *m/e* (rel intensity), 574 (2.6), 572 (2.7), 558 (2.1), 556 (2.1), 540 (3.2), 469 (5.3), 452 (9.2), 451 (23), 450 (6.5), 435 (5.0), 364 (4.0), 363 (4.9), 362 (3.1), 361 (4.0), 347 (5.4), 346 (4.3), 345 (3.6), 285 (4.0), 269 (4.4), 257 (5.9), 241 (4.4), 240 (3.7), 239 (5.1), 167 (5.4), 152 (4.2), 105 (100), and 77 (70).

Found: C, 83.39; H, 5.01%; M$^+$ 574. Calcd for $C_{40}H_{30}O_4$: C, 83.60; H, 5.26%; M, 574.

5-Benzoyl-6-(1-hydroxy-2-oxo-1,2-diphenylethyl)acenaphthene (6): A total of 191 mg (4.1%) of crude product was recrystallized from ethanol,[43] giving 144 mg (3.1%) of pure **6** as yellow rods: mp 201.0—204.0 °C (dec/Ar); UV$_{\max}$ (c-C_6H_{12}) 227 (logε 4.68), 253sh (4.17), 292sh (3.90), 304 (3.98), and 320 nm (3.85); (Fluorescence was not detected.); IR 3500 (OH), 3065, 3040, 2915, 2840, 1750 and 1675 (C=O), 1595, 1450, 1415, 1230, 1150, 1025, 840, 775, 730, 710, and 700 cm^{-1}; NMR ($CDCl_3$) δ=7.72—7.56 (3H, m, ArH), 7.36—6.82 (13H, m, ArH), 6.69—6.53 (3H, m, ArH), 5.88 (1H, sharp s, exch., OH), and 3.38 (4H, broad s, 2CH$_2$); MS (250 °C, 75 eV), *m/e* (rel intensity), 468 (38), 364 (33), 363 (100), 346 (12), 286 (10), 285 (21), 262 (23), 257 (30), 186 (23), 165 (24), 152 (15), 105 (90), and 77 (80).

Found: C, 84.64; H, 4.94%; M$^+$ 468. Calcd for $C_{33}H_{24}O_3$: C, 84.59; H, 5.16%; M, 468.

5,6-Dibenzoylacenaphthene (7): A total of 767 mg (21.2%) of crude product was recrystallized from ethanol,[43] giving 612 mg (16.9%) of pure **7** as white needles: mp 209.0—210.0 °C, (lit,[11] mp 207—208 °C); UV$_{\max}$ (c-C_6H_{12}) 236 (logε 4.74), 248sh (4.53), and 316 nm (3.99); (Fluorescence was not detected.); IR 3080, 3040, 2905, 1655 and 1645 (C=O), 1600, 1270, 1230, 940, and 710 cm^{-1}; NMR ($CDCl_3$) δ=7.80—7.70 (4H, m, *o*-CO-PhH), 7.58 (2H, d, *J*=7.1 Hz, *o*-CO-ActH), 7.52—7.20 (6H, m, *m*- and *p*-CO-PhH), 7.35 (2H, broad d, *J*=7.1 Hz, *o*-CH$_2$-ActH), and 3.49 (4H, s, 2CH$_2$); MS (225 °C, 75 eV), *m/e* (rel intensity), 362 (46), 286 (16), 285 (62), 258 (25), 257 (92), 256 (10), 255 (14), 228 (16), 227 (23), 226 (32), 186 (16), 151 (10), 105 (62), and 77 (100).

(Found: C, 86.62; H, 4.81%).

Reaction of Benzil with n-BuLi–TMEDA Complex. Under an argon atmosphere, *n*-BuLi (25.3 mmol in 11 cm^3 of hexane) and TMEDA (4 cm^3, 26.6 mmol) were introduced into a four-necked 200 cm^3-flask, the mixture was stirred for 15 min, and then 35 cm^3 of dry ether was added to the mixture . To this solution a solution of benzil (2.150 g, 10.23 mmol in 50 cm^3 of ether) was added dropwise over a period of 30 min at −10—0 °C. The yellowish orange solution which resulted was stirred at −10—0 °C for 1 h and for 0.5 h without cooling, and then refluxed for 0.5 h. After the solution was allowed to stand for 30 min, it was hydrolyzed with aqueous ammonium chloride (15 g/50 cm^3). The organic layer was separated, washed with aqueous concd sodium chloride, dried ($MgSO_4$), and evaporated to dryness. The residue was recrystallized from 10 cm^3 of hexane, giving 1.401 g (42.0%) of crude **18a** (mp 118—120 °C). The filtrate was chromatographed on a silica-gel column (100 g) with hexane, benzene, and chloroform as successive eluents, giving 1.387 g of a mixture of **18a** and **18b** as a yellow oil, 44 mg (2.0%) of almost pure benzoin (mp 130—133 °C), and then 213 mg (7.7%) of crude **19** (mp 108—118 °C). The oily mixture was dissolved in 3 cm^3 of hexane and allowed to stand; it gave 145 mg (4.3%) of crude **18a** (mp 119—121 °C). The filtrate of this operation was chromatographed on a silica-gel column (120 g) with hexane–benzene as eluent, giving 743 mg (22.3%) of 1 : 4 mixture of **18a** and **18b** as a colorless solid: mp 76.0—84.0 °C (found: C, 80.98; H, 9.36%); UV$_{\max}$ (c-C_6H_{12}) 253 (logε 2.50), 259 (2.59), and 265 nm (2.41); IR 3535 (OH), 3095, 3060, 3035, 2960, 2865, 1445, and 1150 cm^{-1}; NMR ($CDCl_3$) δ=7.14 (10H, broad s, PhH), 2.55 (1.6H, s, exch., OH of **18b**), 2.22 (0.4H, s, exch., OH of **18a**), 2.32—1.43 (4H, m), and 1.30—0.64 (14H, m).

(5R*, 6R*)- or (5R*, 6S*)-5,6-Diphenyl-5,6-decanediol (18a): A total of 1.546 g (46.3%) of crude product was recrystallized from hexane, giving 1.341 g (40.2%) of pure **18a** as colorless prisms: mp 121.0—122.0 °C; UV$_{\max}$ (c-C_6H_{12}) 218sh (logε 4.13), 253sh (2.47), 259 (2.62), and 265 nm (2.50); IR 3600 (OH), 3055, 3035, 2955, 2930, 2865, 1445, and 1160 cm^{-1}; NMR ($CDCl_3$) δ=7.19 (10H, s, PhH), 2.22 (2H, s, exch., 2OH), 2.47—2.15 (2H, m), 1.77—1.48 (2H, m), and 1.36—0.70 (14H, m); MS (150 °C, 20 eV), *m/e* (rel intensity), 326 (1.5), 309 (0.9), 292 (0.8), 164 (14), 163 (100), 162 (58), 120 (5), 107 (5), 105 (3), 85 (5), 71 (1.3), 57 (6), and 43 (1.4).

Found: C, 80.93; H, 9.53%; M$^+$ 326. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26%; M, 326.

1,2-Diphenyl-1,2-hexanediol (19): The crude product was recrystallized from hexane, giving 131 mg (4.7%) of pure **19** as white hair-like needles: mp 123.0—124.0 °C; UV$_{\max}$ (c-C_6H_{12}) 253 (logε 2.51), 259 (2.59), and 264 nm (2.48); IR 3410 and 3355 (OH), 3065, 3035, 2940, 2865, 1450, and 1040 cm^{-1}; NMR ($CDCl_3$) δ=7.16—6.80 (10H, m, PhH), 4.77 (1H, d, *J*=3.9 Hz, CH), 2.51 (1H, d, *J*=3.9 Hz, exch., OH), 2.49 (1H, s, exch., OH), 2.13—1.97 (2H, m), and 1.47—0.77 (7H, m); MS (135 °C, 23 eV), *m/e* (rel intensity), 270 (0.7), 252 (0.7), 213 (0.7), 195 (1.8), 164 (18), 163 (100), 145 (2), 120 (3), 108 (5), 107 (11), 105 (8), 103 (4), 85 (13), 79 (8), 77 (4), 71 (4), 57 (17), 43 (4), and 41 (3).

Found: C, 79.99; H, 8.12%; M$^+$ 270. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20%; M, 270.

Oxidative Homo-coupling of **3**. *1,2,7,8-Tetrahydrodicyclopenta[cd : lm]perylene (10).* *A)* **3** *: PQ (1/2)*: To a solution of **3** (5.00 mmol in 150 cm^3 of ether), 9,10-phenanthrenequinone (2.154 g, 10.3 mmol) was added with gentle stirring over a period of 5 min at −10—0 °C. The dark green suspension which resulted was stirred for 1 h at −10—0 °C and for 1 h without cooling. Aqueous iron(III) chloride (30 g/100 cm^3) was then added to the supension. After 0.5 h of stirring, the dark brown solid which had precipitated was filtered off with 10 g of Celite and washed with water and ether. The combined filtrate was separated and the organic layer was washed with aqueous concd sodium chloride, dried ($MgSO_4$), and evaporated. The residue was then chromatographed on a silica-gel column (150 g) with benzene as eluent, giving

472 mg of PQ. The residue containing Celite was exhaustively extracted with hot benzene. This extract was dried ($MgSO_4$), concentrated, and chromatographed on a silica-gel column (150 g) with benzene as eluent, giving 205 mg (26.9%) of crude **10** (mp 335—337 °C (dec/Ar)) and then 1.011 g of PQ. Total recovery of the quinone was 68.8%. The crude **10** was recrystallized from benzene, giving 180 mg (23.7%) of pure **10** as brilliant red rods: mp 345.0—346.0 °C (dec/Ar); UV_{max} (c-C_6H_{12}) 382 (logε 3.78), 402 (4.27), 426 (4.64), 443sh (4.41), 450sh (4.66), and 455 nm (4.82), (C_6H_6) 386 (3.70), 407 (4.18), 431 (4.56), and 460 nm (4.69); $Fluorescence_{max}$ (c-C_6H_{12}) 462 (rel intensity 100), 489 (87), 524 (20), and 565 nm (3) (excitation at 450 nm), (C_6H_6) 470 (100), 495 (100), and 530 nm (29) (excitation at 455 nm); IR 3065, 3030, 2905, 2830, 1620, 1585, 1395, 1375, 840, and 815 cm^{-1}; NMR (CS_2) δ= 7.76 (4H, d, J=7.5 Hz, m-CH_2–ArH), 7.09 (4H, broad d, J=7.5 Hz, o-CH_2–ArH), and 3.31 (8H, s, 4CH_2); MS (200 °C, 70 eV), m/e (rel intensity), 304 (100), 303 (33), 302 (19), 301 (18), 300 (17), and 276 (6); $m/2e$, 152 (12), 151.5 (8), 151 (11), 150.5 (10), 150 (17), and 149.5 (3); $m/3e$, 101.7 (0.2), 101.3 (0.3), 101 (0.1), 100.7 (0.8), 100.3 (0.8), and 100 (1.8).

Found: C, 95.13; H, 5.15%; M^+ 304. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30%; M, 304.

B) 3 : PQ (1/1): This was carried out exactly as described above for run *A*), except that 1.077 g (5.17 mmol) of PQ was used. The consumption-ratio of **3** changed as follows: 59% (5 min), 67% (50 min), and 76% (2 h). Column-chromatography gave 150 mg (19.7%) of **10** and 665 mg (61.7%) of PQ.

C) 3 : PQ (1/1) with Acetolysis: This was carried out exactly as described for run *A*), except that 1.070 g (5.14 mmol) of PQ was used and that the reaction mixture was treated with acetic anhydride (45 cm^3, 0.48 mol) and pyridine (5 cm^3), and then with 100 cm^3 of dil hydrochloric acid. After the addition of PQ, the consumption-ratio of **3** and the color of the reaction mixture changed as follows: 3—60 min, 65%, dark green; 2—4 h, 73—82%, dark green and partly dark yellow: 5—6 h, 86—87%, dark yellow. Column-chromatography gave 207 mg (27.2%) of **10** and then 703 mg (47.8%) of crude **11**. The latter was recrystallized from benzene, giving 619 mg (42.1%) of pure 9,10-diacetoxyphenanthrene (**11**); mp 203.0—204.0 °C, (lit,[12] mp 203—203.5 °C); IR 3075, 2930, and 1785 and 1770 cm^{-1} (C=O); NMR ($CDCl_3$) δ=8.75—8.56 (2H, m), 7.95—7.78 (2H, m), 7.78—7.50 (4H, m), and 2.46 (6H, s).

(Found: C, 73.20; H, 4.72%).

D) 3 : PQ (1/2) in the Presence of Cyclooctene: Freshly distilled cyclooctene (from sodium wire) (50 cm^3) was added to a solution of **3** (5.00 mmol in 150 cm^3 of ether) and the mixture was treated with PQ (2.195 g, 10.5 mmol) as described for run *A*). Column-chromatography gave 200 mg (26.3%) of **10** and 1.64 g (73.5%) of PQ.

E) 3 : $CoCl_2$ (1/2): Anhydrous cobalt(II) chloride[41b] (1.580 g, 12.2 mmol) was dried at 120 °C/0.1 mmHg for 4 h, and then added to a solution of **3** (5.00 mmol in 150 cm^3 of ether) over a period of 15 min at −78 °C . During 1 h of stirring, the solution became pale brown and *ca.* 10% of **3** was consumed. The reaction mixture was then allowed to come to room temperature gradually; after 2 h, $\geq$95% of **3** was consumed. The black suspension which resulted was treated as described for run *A*), giving 210 mg (27.6%) of **10**.

F) 3 : 2,3-Dibromo-1,4-naphthoquinone (1/1): This was carried out exactly as described for run *A*), except that 1.617 g (5.12 mmol) of the quinone[44] was used. The consumption-ratio of **3** and the color changed as follows: 3 min, 94%, brown purple; 20 min, 98%, blue green; 1—2 h, 98%, dark green. Column-chromatography gave 40 mg (5.2%) of **10**.

G) 3 : 2,3-Dichloro-5,6-dicyano-1,4-benzoqinone (1/1): This was carried out as described for run *A*), except that 1.160 g (5.11 mmol) of the quinone[41d] was used and that the reaction mixture was refluxed for additional 1 h. Finally, approximately 50% of **3** was consumed and 76 mg (10%) of **10** was obtained.

The authors wish to thank Professor S. Aoyagi (Tokyo Institute of Technology) for the measurements of the cyclic voltammograms. We also would like to thank Professor Y. Sasada and Dr. A. Takenaka (Tokyo Institute of Technology, Nagatsuta) for their helpful discussions.

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