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Denisio Masaharu Togashi [a], David Ernest Nicodem* [a], Roberto Marchiori [a] & Maria Luisa P. de F. C. Marchiori [a]

[a] Instituto de Quimica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil, 21945-970 E-mail:
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SYNTHESIS OF 9,10-PHENANTHRENEQUINONES BY PHOTOCYCLIZATION OF DERIVATIVES OF BENZOINS: SCOPE AND LIMITATION OF THE METHODOLOGY

Denisio Masaharu Togashi, David Ernest Nicodem*,

Roberto Marchiori, and Maria Luisa P. de F. C. Marchiori

Instituto de Quimica, Universidade Federal do Rio de Janeiro
Rio de Janeiro, Brazil, 21945-970
e-mail : NICODEM@iq.ufrj.br

Abstract: Symmetric 9,10-phenanthrenequinones with methyl, methoxy, and chloro substituents at the 3 and 6 positions have been synthesized by photocyclization of 4,5-bis-(aryl)-2-phenyl-1,3,2-dioxaboroles and 2,3-diaryldioxenes followed by oxidative hydrolysis.

Phenanthrenequinones are a class of compounds with biological activity[1] and there is current interest in their synthesis. There are a number of synthetic routes available[2-8] but the most used procedure involves the oxidation of phenanthrenes[2-4], which can be obtained by the photochemical cyclization of stilbenes[9,10], as shown in figure 1. This route often gives low yields in the cyclization step due to competing *cis-trans* isomerization[9,10]. It is also difficult to oxidize phenanthrenes to phenanthrenequinones in high yields[2-4].

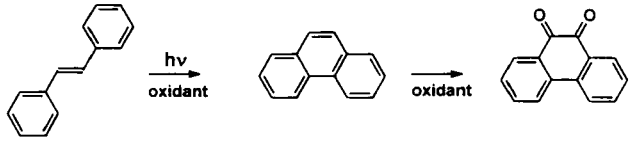

Figure 1 - Principal path for phenanthrenequinone preparation.

An alternative synthesis, shown in figure 2, surmounts these problems. The required benzoins are well known[11] and the photocyclization does not suffer from competing *cis-trans* isomerization. Hydrolysis of the resulting 9,10-dioxophenanthrene leads to the hydroquinone which is easily oxidized by molecular oxygen to the quinone[12].

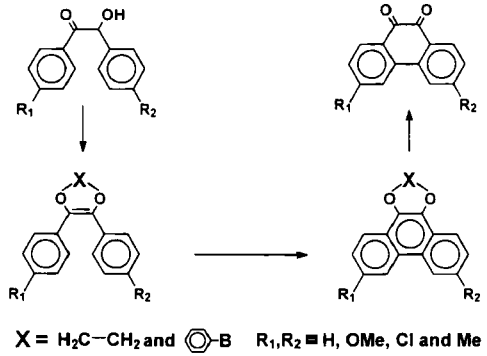

Figure 2 - Alternative phenanthrenequinone synthesis.

This methodology has been applied using benzeneboronic acid and benzoin to give 2,4,5-triphenyl-1,3,2-dioxaborole (**1**), shown to photocyclize in good yield to 9,10-phenanthrenequinone (**5**)[7]. Phosgene has also been used with both benzoin and 4,4'-dimethoxybenzoin[8]. References to the use of other enolization reagents or substrates to generate *cis*-stilbenediol templates followed by photocyclization could not be found. Since we required symmetrical phenanthrenequinones for photochemical studies, we decided to test this methodology using benzeneboronic acid, for a series of symmetrical benzoins having both electron donating (methoxy and methyl) and electron withdrawing

(chloro) groups in order to test the generality and/or limits to the use of this reagent. The use of ethylene glycol was also proposed as an alternative enolization reagent.

Results and Discussion

Synthesis of the dioxaboroles: The benzoins used in this study were all known compounds and were synthesized from the corresponding benzaldehydes using literature methods[11]. The benzeneboronic acid was prepared by the Grignard reaction of phenyl magnesium bromide with methyl borate using the literature procedure[13].

Reaction of benzeneboronic acid with a stoichiometric quantity of the corresponding benzoin in refluxing toluene, with removal of water, gave the corresponding dioxaboroles. The yields of product are shown in table 1. The yields of crude product are all around 90%. In the case of the dimethyl derivative (**4**) where only the recrystallized yield was obtained the yield is still high. All these compounds, except dioxaborole **1**[14] are unknown to the literature.

Table 1 - Results of the dioxaborole preparations

Dioxaborole	*Yields(%)*	*M.P. (^{0}C)*
1 (R_1,R_2=H)	91	112-3
2 (R_1,R_2=OMe)	93	122-3
3 (R_1,R_2=Cl)	88	140-2
4 (R_1,R_2=Me)	73	139-40

Dioxaboroles are more stable towards hydrolysis and oxidation than boronate esters and borates, and this stability may by due to the increased aromatic character of the 5 member ring and increased electron density on boron which would decrease the rate of nucleophilic attack[14]. Even so, crystalline **1** was found to degrade and became yellow upon prolonged stored (weeks) at room temperature. All the derivatives synthesized (**2-4**) showed similar yellowing with time even when stored under an atmosphere of dry nitrogen. This known degradation[14] could be avoided if the compounds were stored under

vacuum. However, the rate of degradation was sufficiently slow so that special techniques were not required for manipulation.

Cyclization of the dioxaboroles: The oxidative photocylization of stilbenes to phenanthrenes is commonly carried out in the presence of oxygen with a catalytic amount of iodine[9]. This procedure often gives low yields of phenanthrene and alternate oxidants have been sought. One recent method uses a stoichiometric amount of iodine in the presence of an excess of propylene oxide to remove the hydrogen iodide formed[10]. Diphenyldiselenide has also been used as the oxidizing agent when 1 was photocyclized[7]. The use of iodine and air did not give us satisfactory yields of cyclization and the milder oxidizing agent, diphenyldiselenide was then tried. It was found that the phenanthrene diol esters initially formed were very sensitive to hydrolysis and oxidation giving the corresponding phenanthrenequinones as a significant byproduct. Therefore base was added to the reaction mixture prior to work up and all the phenanthrenediol esters were allowed to hydrolyze and oxidize to the quinones. The results are shown in table 2.

Table 2 - Results of phenanthrenequinone synthesis

Phenanthrenequinone	*Irradiation time (hr.)*	*Yields (%)*	*M.P. (°C)*
5 (R_1,R_2=*H*)	2,8	54	209-10
6 (R_1,R_2=*OMe*)	2,5	47	233-4
7 (R_1,R_2=*Cl*)	3,0	57	270(subl.)
8 (R_1,R_2=*Me*)	2,6	53	212-4

The substituents used here, which included both electron donating and withdrawing groups, did not alter the rate or yield of cyclization, or the ease of hydrolysis, indicating that this is a useful general procedure requiring only two synthetic steps from the benzoin to the phenanthrenequinone.

Given the difficulties associated with the storage of the dioxaboroles and the reactivity of the phenanthrenediol esters toward hydrolysis, a more stable derivative was sought. Since the reaction of benzoin with ethylene glycol to produce 2,3-diphenyl-1,4-

dioxene (**9**) was known[15], this reaction was extended to substituted benzoins. The scheme then involves the photocyclization of the dioxenes to the corresponding phenanthrenediol diether followed by oxidative hydrolysis giving the corresponding 9,10-phenanthrenequinone.

Synthesis of the dioxenes: 2,3-Diphenyl-1,4-dioxene **9** was prepared by two literature methods[15] (figure 3). In Procedure A, the ketal **9a** was initially formed by refluxing benzoin with ethylene glycol in benzene using *p*-toluenesulfonic acid as catalyst and with the removal of water. The ketal **9a** was then rearranged to the dioxene **9** at higher temperature using the same acid catalyst and with the removal of water. Using Procedure B, the dioxene **9** was obtained directly by the reaction of the benzoin with ethylene glycol using *p*-toluenesulfonic acid as catalyst at higher temperature. A third procedure (C) was used with 4,4'-dichlorobenzoin. In this case the ditosylate of ethylene glycol was added to 4,4'-dichlorobenzoin using a biphasic media and a phase transfer catalyst was used.

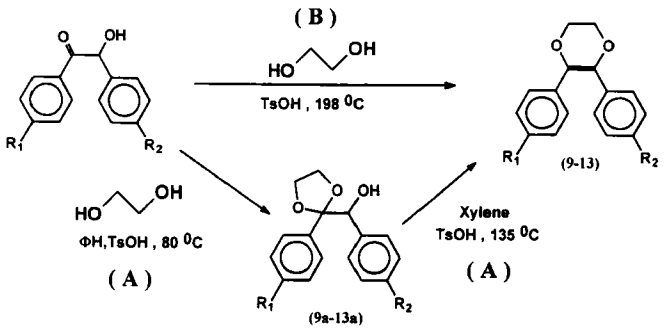

Figure 3 - Dioxene synthesis.

In procedure A, the addition of ethylene glycol to the benzoin gave generally good yields of the corresponding ketal, except for 4,4-dimethoxybenzoin where no ketal formation was observed. In this case, the initial reaction conditions gave a yield of 65% of the dioxene **10**. It is interesting to observe that 4-methoxybenzoin gives a good yield of ketal **13a**.

The direct reaction in ethylene glycol (Procedure B) gave low yields of dioxenes **9** and **12** when benzoin or 4,4'-dimethylbenzoin was used (yields of 35% and 14% respectively) so this procedure was not used for the other benzoin derivatives.

Table 3 - Results of the synthesis of the 2,3-diaryl-*p*-dioxenes using different procedures.

Dioxene	*PROCEDURE (Yield %)*		
	A[†]	*B*	*C*
9 *(R_1,R_2=H)*	24	35	?
10 *(R_1,R_2=OMe)*	65*	?	?
11 *(R_1,R_2=Cl)*	0	?	33
12 *(R_1,R_2=Me)*	0*	14	?
13 *(R_1=H,R_2=OMe)*	0	?	?

† The ketal yield was > 90% (except for the case of the dichloro derivative where it was ~ 50%). * No ketal could be detected.

The mechanism proposed by Summerbell and Beger[15] shown in figure 4 explains the observed differences in reactivity. In this mechanism the initially formed ketal rearranges to the dioxene through protonation of the hydroxy group and formation of a benzylic carbocation followed by migration of oxygen. The presence of a *p*-methoxyphenyl group alpha to the forming carbocation accelerates the formation of the cation and reduces the stability of the ketal. The mono methoxy derivative would not show this enhanced reactivity since the ketal **13a** is alpha to the *p*-methoxyphenyl group and the charge develops alpha to the unsubstituted ring.

The dioxene **9** was formed from the respective ketal **9a** in 43% yield but the ketal **11a** did not generate dioxene **11**. It was, however, possible to prepare dioxene **11** using procedure C. The reaction of the ditosylate of ethylene glycol with benzoin in biphasic media is known[16] but had not been used for substituted benzoins. Although yields of the dioxenes were generally low, it was possible to prepare samples of the unsubstituted derivative as well as the dimethoxy, dimethyl, and dichloro derivatives.

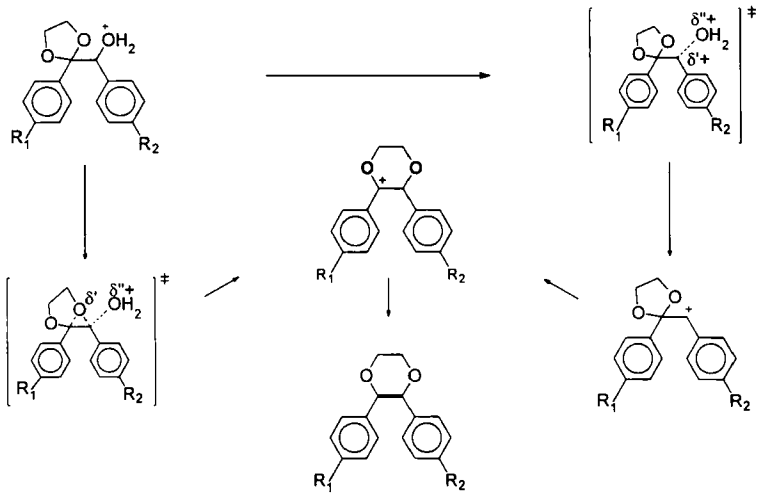

Figure 4 - Benzoin ketal Rearrangements

Photocyclization of the dioxenes: The photocyclization of the dioxenes was initially studied using oxygen and iodine as the oxidant. Although the dioxenes were consumed, the product reaction mixture was complex and phenanthrenes were not obtained. The only isolatable product was the ethylene glycol dibenzoate. This may be due to oxidation at the dioxene double bond in competition with cyclization since treatment of dioxene with *m*-chloroperbenzoic acid[17] or singlet oxygen, gives ethylene glycol dibenzoate in high yields[18]. The use of a stoichiometric quantity of iodine in the absence of oxygen was also unsatisfactory. In a second modification, 2-butylene oxide was added to the iodine to remove hydrogen iodide formed by reduction of iodine (in the literature propylene oxide has been used for this purpose[10]). Under these conditions the reaction was fast and oxidation of the initial reaction mixture with potassium permanganate give a 52% yield of phenanthrenequinone **5** when dioxene **9** was used, and a 26% yield of phenanthrenequinone **6** when the dimethoxy derivative **10** was used. Given the low yields of cyclization and the difficulties in preparation of the dioxenes, this synthetic route was not further explored.

The synthesis of phenanthrenequinones by photocyclization of the dioxenes was not found to be a good synthetic route. The dioxenes are more difficult to synthesize

than the corresponding dioxaboroles and the yields of dioxenes depend greatly on the nature of the substituent. The photocyclization is also more complicated and with lower yields. It is possible that the more electron rich character of the stilbene double bond makes this sensitive to oxidation during the photocyclization. The ether function is also resistant to hydrolysis and strong oxidizing conditions were necessary to transform the dioxaphenanthrene into the corresponding phenanthrenequinone.

Conclusions

Our results show that the methodology used for the synthesis of phenanthrenequinones by the photocyclization of benzeneboronic acid esters of benzoins is insensitive to the effects of electron withdrawing or donating groups in either the ester formation step or the photocyclization and the procedure can be expected to be generally valid as long as the substituents are compatible with the reagents used for esterification, photocyclization and hydrolysis-oxidation.

Experimental

IR spectra were obtained using a Nicolet-FTIR model 764, NMR on a Varian VXR-300 (TMS), MS spectra on a VG Autospec at 70 eV, and elemental analysis utilized a Perkin-Elmer 2400 CHN. Reagents and solvents were analytical grade unless otherwise stated.

Benzoin synthesis: The benzoins used as starting materials were all synthesized following literature procedures[11] and gave products with melting points and spectral properties consistent with the literature and their structure[19].

Synthesis of the dioxaboroles: The literature methodology[14] for the synthesis of 2,4,5-triphenyl-1,3,2-dioxaborole (**1**) was employed. The substituted compounds were not found in the literature. In the procedure, the Benzeneboronic acid[13] and the benzoin were dissolved in toluene, then heated to reflux for 4 hours in a 250 ml round bottom flask equipped with a Dean-Stark tube and reflux condenser. Water was removed as necessary. The toluene was then removed, under vacuum, and the resulting solid recrystalized in n-hexane and stored in evacuated and sealed ampoules.

2,4,5-Triphenyl-1,3,2-dioxaborole (1): 4.84 g of benzeneboronic acid and 8.48 g of benzoin in 150 ml of toluene gave 10.8 g (91%) of product; mp 112-3 ^{0}C (lit[14] 112 ^{0}C). IR (KCl) C=C 1604 cm^{-1}, B-O 1367 cm^{-1}; H-NMR ($CDCl_3$): d (ppm) 8.39 (d, 2H, J= 7.14 Hz), 8.01 (d, 4H, J=7.23 Hz), 7.85-7.76 (m, 3H), 7.72-7.64 (m, 6H). M^+ : 298 (100%). Calcd. for $C_{20}H_{15}BO_2$: C, 80.57%; H, 5.07%. Found: C, 79.91%; H, 5.00%.

4,5-Bis(4-methoxyphenyl)-2-phenyl-1,3,2-dioxaborole (2): 4.84 g of benzeneboronic acid and 10.88 g of 4,4'-dimethoxybenzoin in 150 ml of toluene gave 13.2 g (93%) of

product; mp 122-3. IR (KCl) : C=C 1605 cm^{-1}, B-O 1367 cm^{-1}. H-NMR ($CDCl_3$) : δ (ppm) 8.35 (d, 2H, J= 6.51 Hz), 7.90 (d, 4H, J=8.76 Hz), 7.82-7.33 (m, 3H), 7.21 (d, 4H, J=8.79 Hz), 4.12 (s, 6H). M^+ : 358 (100%). Calcd. for $C_{22}H_{21}BO_4$: C, 73.77%; H, 5.35%. Found: C, 74.01%; H, 5.39%.

4,5-Bis(4-chlorophenyl)-2-phenyl-1,3,2-dioxaborole (3): 2.42 g of benzene boronic acid and 5.62 g of 4,4'-dichlorobenzoin in 75 ml of toluene gave 6.4 g (88%) of product; mp 140-2. I.R (KCl):C=C 1605 cm^{-1}, B-O 1366 cm^{-1}. H-NMR ($CDCl_3$) : δ (ppm) 8.31 (d, 2H, J= 6.87 Hz), 7.86 (d, 4H, J=8.49 Hz), 7.81-7.73 (m, 3H), 7.64 (d, 4H, J=8.40 Hz). M^+:366 (100%). Calcd. for $C_{20}H_{13}Cl_2BO_2$: C, 65.45%; H, 3.57%. Found: C, 64.87%; H, 3.58%.

4,5-Bis(4-methylphenyl)-2-phenyl-1,3,2-dioxaborole (4): 3.25 g of benzene boronic acid and 6.02 g of 4,4'-dimethylbenzoin in 75 ml of toluene gave 6.3 g (73%) of product; mp 139-40. IR (KCl) : C=C 1600cm^{-1}, B-O 1360 cm^{-1}. H-NMR ($CDCl_3$) : δ (ppm) 8.03 (d, 2H, J= 6.30 Hz), 7.56 (d, 4H, J=8.40 Hz), 7.51-7.40 (m, 3H), 7.16 (d, 4H, J=8.40 Hz), 2.36 (s, 6H). M^+ : 326 (100%). Calcd. for $C_{22}H_{21}BO_2$: C, 81.01%; H, 5.87%. Found: C, 79.36%; H, 5.86%.

Synthesis of 9,10-phenanthrenequinones from dioxaboroles: The photochemical cyclizations were carried out in a 2 liter Pyrex reactor containing a double wall quartz well in which was placed a 450 W medium pressure Hanovia mercury lamp. The reactor also contained an inlet for gas and outlets for a reflux condenser and sampling port.

As a general procedure, 5 mmol of dioxaborole and 5.0 mmol of diphenyl diselenide were dissolved in 1liter of benzene and placed in the reactor. Dry argon was bubbled for 30 min. then irradiation was initiated while continuing to pass argon. The solution was irradiated for 150 to 180 min. The organic phase was then washed with 100 ml portions of 1 M sodium hydroxide. Upon addition of the NaOH it was observed that the color of the organic phase changed from yellow to orange and the aqueous base took on a yellow color. The organic phase was washed with NaOH three times or until the aqueous solution remained clear. The organic phase was washed with a 3x100 ml portions of aqueous 5% hydrochloric acid, dried with anhydrous sodium sulfate, then evaporated at reduced pressure giving an orange oil. This oil was dissolved in chloroform which was allowed to evaporate. The resulting oil was triturated with successive 100 ml portions of n-hexane until TLC analysis indicated that diphenyl diselenide was no longer present in the hexane extracts. The residue was then recrystalized from acetic acid.

9,10-phenanthrenequinone (5): 1.49 g (5 mmol) of dioxaborole **1** gave 0.56 g (54%) of product upon irradiation for 170 min. mp 209-10 °C (lit.[7] 204-8); IR (KCl) : C=O 1674cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 8.13 (d, 2H, J= 7.65 Hz), 7.96 (d, 2H, J=7.92 Hz), 7.67 (t, 2H, J=7.69Hz), 7,43 (t, 2H, J=7,54 Hz). M^+ : 208.

3,6-dimethoxy-9,10-phenanthrenequinone (6): 1.79 g (5 mmol) of dioxaborole **2** gave 0.63 g (47%) of product upon irradiation for 150 min. mp 233-4 °C (lit.[8] 229-32); IR (KCl) : C=O 1655cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 8.16 (d, 2H, J= 8.70 Hz), 7.35 (d, 2H, J=2.37 Hz), 6.94 (dd, 2H, J=8.75Hz) , 3.96 (s, 6H); M^+ : 268; Calcd. for $C_{16}H_{12}O_2$: C, 71.64%; H, 4.51%. Found: C, 72.00%; H, 4.55%.

3,6-dichloro-9,10-phenanthrenequinone (7): 1.83 g (5 mmol) of dioxaborole **3** gave 0,79 g (57%) of product upon irradiation for 180 min. mp < 270 °C (sub.) (lit.[20] 295 dec.); IR (KCl) : C=O 1679cm^{-1}; H-NMR ($CDCl_3$): d (ppm) 8.13 (d, 2H, J=8.39 Hz), 7.92 (d, 2H, J=1.78 Hz), 7.46 (dd, 2H, J=8.35Hz); M^+ : 276; Calcd. for $C_{14}H_6O_2$: C, 60.68%; H, 2.18%. Found: C, 60.90%; H, 1.98%.

3,6-dimethyl-9,10-phenanthrenequinone (8): 1.83 g (5 mmol) of dioxaborole **4** gave 0,62 g (53%) of product upon irradiation for 156 min. mp 212-4 °C (lit.[5] 216); IR (KCl) : C=O 1673cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.86 (d, 2H, J= 7.95 Hz), 7.52 (s, 2H), 7.11 (dd, 2H, J=7.93Hz), 2.41 (s, 6H); M^+ : 236; Calcd. for $C_{14}H_{12}O_2$: C, 81.34%; H, 5.12%. Found: C, 81.83%; H, 5.01%.

Synthesis of dioxenes: Two methods were used, formation and rearrangement of the ketal (Procedure A), and acid catalylised direct cyclization (Procedure B). Additionally, dioxene **12** was prepared by procedure C. All the recristalized products (dioxenes and ketals) showed only a single spot on TLC (silica, and elution with chloroform).

PROCEDURE A:

2-Phenyl-α-hydroxybenzyl-1,3-dioxolane (9a): 10.3 g of benzoin, 20.2 g of ethylene glycol, and 0.112 g of *p*-toluenesulfonic acid were dissolved in benzene in a 250 ml round bottom flask equipped with a Dean-Stark tube and reflux condensor. The mixture was refluxed for 20 hr with periodic removal of water. The cooled mixture was then extracted with water, dried with $CaCl_2$, and the solvent removed under vacuum giving 12.1 (97%) of a white solid. Recrystalization in ethanol resulted in a mp of 140-2°C (lit[15] 141). IR (KCl) : O–H 3440 cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.13-7.25 (m, 10H), 4.89 (d, 1H, J= 2,73 Hz), 4.03-4.07 (m, 2H), 3.81-3.86 (m, 2H), 2.85 (d, 1H, J= 2,96 Hz)[21]; Calcd. for $C_{16}H_{16}O_3$: C, 74.98%; H, 6.29%. Found: C, 75.16%; H, 6.33%.

2,3-Bisphenyl-1,4-dioxene (9): 7.0 g of the ketal **9a** and 0.2 g of *p*-toluenesulfonic acid were dissolved in 100 ml of xylene in a 250 ml round bottom flask equipped with a Dean Stark tube and reflux condenser. The mixture was refluxed for 15 hr, with periodic removal of water. The cooled mixture was then washed with water, and the xylene removed at reduced pressure. The resulting solid was recrystalized in ethanol yielding 3.0 g (43%) of product **9**. mp 95-6°C (lit[15] 98). IR (KCl) : C=C 1630 cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.20 (m, 10H), 4.29 (s, 4H); M^+ : 238. Calcd. for $C_{16}H_{14}O_2$: C, 80.65%; H, 5.92%. Found: C, 81.01%; H, 6.01%.

2,3-Bis(4-methoxyphenyl)-1,4-dioxene (10)[22]: 27.23 g of 4,4'-dimethoxybenzoin, 18.62 g of ethylene glycol, and 0.50 g of *p*-toluenesulfonic acid were dissolved in 300 ml of benzene in a 500 ml round bottom flask equipped with a Dean-Stark tube and reflux condensor. The mixture was refluxed for 24 hr with periodic removal of water. The solvent was removed under vacuum giving an oil which was dissolved in ethanol and crystallized giving 19.5 g (65.4%) of a white solid with a mp of 107-8°C; IR (KCl) : C=C 1640cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.16 (dd, 4H, J=7.36), 7.14 (d, 4H, J=7.85), 4.28 (s, 6H), 3.75 (s, 6H); M^+ :298. Calcd. for $C_{18}H_{18}O_4$: C, 72.46%; H, 6.08%. Found: C, 72.49%; H, 6.08%.

2- (*p*-Chlorophenyl)- α-hydroxy (*p*-chlorobenzyl) -1,3-dioxolane (11a): 3.3 g of 4,4'-dichlorobenzoin, 3.0 g of ethylene glycol, and 0.05 g of *p*-toluenesulfonic acid were dissolved in 60 ml of benzene in a 125 ml round bottom flask equipped with a Dean-

Stark tube and reflux condensor. The mixture was refluxed for 23 hr with periodic removal of water. The solvent was removed under vacuum giving an oil which crystallized giving 2.0 g (50%) of an off white solid. Recrystalization in ethanol resulted in white crystalline solid with a mp of 125-6^{0}C. IR (KBr) : O–H 3477 cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.04-7.22 (m, 8H), 4.82 (br s, 1H), 4.05-4.07 (m, 2H), 3.80-3.85 (m, 2H), 2.83 (br s, 1H)[21]; Calcd. for $C_{16}H_{14}O_3Cl_2$: C, 59.09%; H, 4.34%. Found: C, 59.79%; H, 4.23%.

2,3-Bis(4-chlorophenyl)-1,4-dioxene (11): 1.53 g of the ketal **11a** and 0.05 g of *p*-toluenesulfonic acid were dissolved in 60 ml of xylene in a 125 ml round bottom flask equipped with a Dean Stark tube and reflux condenser. The mixture was refluxed for 18 hr, with periodic removal of water. The xylene was then removed at reduced pressure giving an oil. This was recrystalized in ethanol yielding 1.45 g (95%) of product, mp 122-5^{0}C. After a second recrystalization the melting point was 125-6^{0}C. Its infrared spectra was the same as the ketal reagent **(11a)**.

2 - (*p*-Metoxyphenyl) - α- hydroxybenzyl - 1,3-dioxolane (13a): 6.05 g of 4-methoxy benzoin, 1.55 g of ethylene glycol, and 0.10 g of *p*-toluenesulfonic acid were dissolved in 150 ml of benzene in a 500 ml round bottom flask equipped with a Dean-Stark tube and reflux condensor. The mixture was refluxed for 24 hr with periodic removal of water. The cooled mixture was washed with aqueous sodium bicarbonate, dried ($CaCl_2$) and the solvent was then removed under vacuum giving a solid which was dissolved in ethanol and crystallized giving 6.8 g (93%) of white crystals with a mp of 105-6°C; IR (KCl) : O–H 3450 cm^{-1}, C=C 1610 cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.09-7.21 (m, 7H), 6.75 (d, 2H, J= 8.83 Hz), 4.86 (br s, 1H) 3,98-4.11 (m, 2H), 3.80-3.89 (m, 2H), 2.83 (br s, 1H)[21]; Calcd. for $C_{17}H_{18}O_4$: C, 71.31%; H, 6.34%. Found: C, 71.32%; H, 6.37%.

2-phenyl,3-(4-methoxyphenyl)-1,4-dioxene (13): 1.43 g of the ketal **13a** and 0.05 g of *p*-toluenesulfonic acid were dissolved in 60 ml of xylene in a 125 ml round bottom flask equipped with a Dean Stark tube and reflux condenser. The mixture was refluxed for 20 hr. The solvent was removed at reduced pressure giving an oil which would not crystalize.

PROCEDURE B:

2,3-Bisphenyl-1,4-dioxene (9): Following the literature procedure[15], 45.1 g of benzoin and 0.5 g of *p*-toluenesulfonic acid in 250 ml of ethylene glycol was heated at reflux for 24 hr. The cooled solution was diluted with 300 ml of ice water and stirred for 1 hr. A yellow oil separated, which was extracted diethylether. Evaporation of the ether at reduced pressure gave 15.6 g of straw yellow crystals. Recristalization from ethanol gave a white solid with a mp of 95-6^{0}C. (35 %)

2,3-Bis(4-methylphenyl)-1,4-dioxene (12): 7.1 g of 4,4'-dimethylbenzoin, 50 ml of ethylene glycol, and 0.10 g of *p*-toluenesulfonic acid, were placed in a 125 ml round bottom flask equipped with a reflux condenser. The mixture was heated at reflux for 24 hr, cooled, and added to 200 ml of ice water which caused an oil phase to separate. This mixture was stirred for 1 hr then extracted with diethylether. The ether phase was dried ($CaCl_2$) and evaporated under vacuum giving a straw yellow solid (5.3 g) which was recrystalized from ethanol and identified[23] as starting 4,4'-dimethylbenzoin. A second recrystalization of the mother liqueur gave 1.1 g (14%) of product having a mp of 103-

5°C; IR (KCl) : C=C 1630cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.12 (dd, 4H, J= 6.42Hz), 6.96 (d, 4H, J=7.98 Hz), 4.30 (s, 4H), 2.27 (s, 6H); M^+ : 266. Calcd. for $C_{18}H_{18}O_2$: C, 81.17%; H, 6.76%. Found: C, 81.06%; H, 6.86%.

PROCEDURE C:

2,3-Bis(4-chlorophenyl)-1,4-dioxene (11): Following the literature procedure[16], 2.81 g of 4,4'-dichlorobenzoin, 3.70 g of ethylene glycol ditosylate, 0.06 g of tetrabutylamonium bromide, 15 ml of a 33% aqueous solution of sodium hydroxide, and 90 ml of benzene were placed in a 250 ml round bottom flask equipped with a reflux condenser. The mixture was heated at reflux for 14 hr under a slow stream of nitrogen. The cooled solution was separated into aqueous and organic phases, the organic phase was washed with 6 N hydrochloric acid, dried with $CaCl_2$ and evaporated under reduced pressure. The resulting oil was crystallized from ethanol giving 1.0 g (32.6%) of white crystals (**11**) with a mp of 118-9°C. IR (KCl) : C=C 1625cm^{-1}; H-NMR ($CDCl_3$) : δ (ppm) 7.15 (s, 8H), 4.30 (s, 4H); M^+ : 306. Calcd. for $C_{16}H_{12}O_2Cl_2$: C, 62.56%; H, 3.94%. Found: C, 63.31%; H, 3.65%.

Synthesis of 9,10-phenanthrenequinones from dioxenes: The photochemical cyclizations were carried out in the same system previously described. 5 mmol of the appropriate dioxene, 5 mmol (1.27 g) of iodine, and 43 ml of 2-epoxy-butane were dissolved in 1 l of benzene and placed in the reactor. Argon was bobbled through the solution during the irradiation. Irradiation times were 2 hr. for 9,10-phenanthrenequinone **5** and 3 hr. for 3,6-dimethoxy-9,10-phenanthrenequinone **6** formation. Following irradiation the benzene solution was removed and evaporated under vacuum giving a dark oil. This was dissolved in ethanol and 5 mmol (0.90 g) of $KMnO_4$ was added and the mixture was stirred for 24 hr. 10 ml of concentrated hydrochloric acid was then added and the mixture heated until the dark color had disappeared. Upon concentrating the mixture to half its original volume, yellow crystals formed which were filtered and dried and identified as the corresponding phenanthrenequinone. The yield of phenanthrenequinone **5** was 52% while the yield of phenanthrenequinone **6** was 26%.

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