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Journal of Photochemistry and Photobiology A: Chemistry 138 (2001) 111–122

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Efficient photocycloaddition of phenanthroquinones with simple olefins

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Received 25 July 2000; received in revised form 24 October 2000; accepted 25 October 2000

Abstract

A series of substituted phenanthroquinones (PQ's) was prepared, their phosphorescence spectra and decay rate constants, cyclic voltammograms, and photoreaction in the presence of tetramethylethylene (TME) were investigated. With 450 nm irradiation their triplet excited state cyclized with TME to give the corresponding dioxenes, 2′,2′,3′,3′-tetramethyl-1′,4′-dioxa-1′,2′,3′,4′-tetrahydrotriphenylene, cleanly and much faster than that with 300 nm irradiation. The pattern of the reaction was effected weakly in random fashion by the substituent at the 3-position of PQ's. The photocycloaddition, as exemplified by PQ itself, is so efficient that it occurred even by room light and during optical spectroscopic recordings; its limiting quantum yield in benzene is established to be unity with 450 nm irradiation. It owes the unusual efficiency to a long lifetime of the PQ triplet excited state with the n–$^*\pi$ configuration, and to the successful cyclization in every diffusion controlled collision as implicated by TME quenching of PQ phosphorescence intensity in CCl_4 solution. The triplet excited state reaction was supported by competitive quenching of the dioxene formation by triplet quenchers as well as by oxygen. These PQ's do not fluoresce in solution, but show phosphorescence in solid solution with lifetimes of about 10 ms and in CCl_4 solution with lifetimes in the order of 100 μs in the room temperature range. PQ's with 3-cycano, 3-chloro, 3-methoxy, and without substitutions photocyclized to cyclohexene to give the corresponding dioxenes with small stereochemical scrambles, that was interpreted that the extent of electron transfer in the 1,6-diradical stage is small. Similar photocycloadditions to isobutene gave a 1:1 mixture of two regio-isomers, this was taken as evidence for a direct radical attack on olefins to give 1,6-diradical intermediates. © 2001 Published by Elsevier Science B.V.

Keywords: Excited state cycloaddition; *o*-Quinone triplet state reaction; Stepwise radical reaction; Stereo- and regio-specificity; Charge transfer contribution

1. Introduction

The cycloaddition of *o*-quinones to olefins could be initiated thermally or photolytically [1–16] to produce dioxene derivatives (such as 2′,2′,3′,3′-tetramethyl-1′,4′-dioxa-1′,2′,3′,4′-tetrahydrotriphenylene **4** in Schemes 1 and 2) by a 1,4-addition, but by the latter photolytic initiation it generally gives certain by-products, such as 1,2-addition **5** [4–8] as well as photoreduction products **6** and **7** [9–11] typical to ketone excited state reactions [17]. The reaction has been known for a long time [1] and its synthetic applications and mechanism have been the subject of studies in the 1960's [4–11]. On the basis of stereochemistry and product patterns, the photoreaction of phenanthroquinone (PQ) with olefins is proposed to occur by stepwise radical addition to give dioxene **4** from the triplet excited state [6–11,15,16]. We have discovered that the photoreaction of a series of substitute PQ's with tetramethylethylene (TME) is efficient and clean-dependent on excitation wavelengths. The early investigations have been generally explained by inferring to the ketone triplet state photoreaction, but lack the benefit of newer probing methods available in recent years. In view of the clean reaction pattern, the present reaction system was used to buttress the proposal made in former studies (such as the triplet state reaction and others), and to examine the possibility of electron transfer in the photoreaction. In terms of preparative chemistry, this is an extraordinary efficient triplet carbonyl group reaction. We wish to describe this photoreaction together with some mechanistic studies in this report.

2. Experimental

2.1. Materials and methods

2.1.1. Materials and general methods

Melting points were determined with Mel-Temp instrument by Laboratory Device, USA and uncorrected. The infrared spectra were determined with a Perkin-Elmer 983 spectrophotometer in nujol mulls, mass spectra with a Finni-

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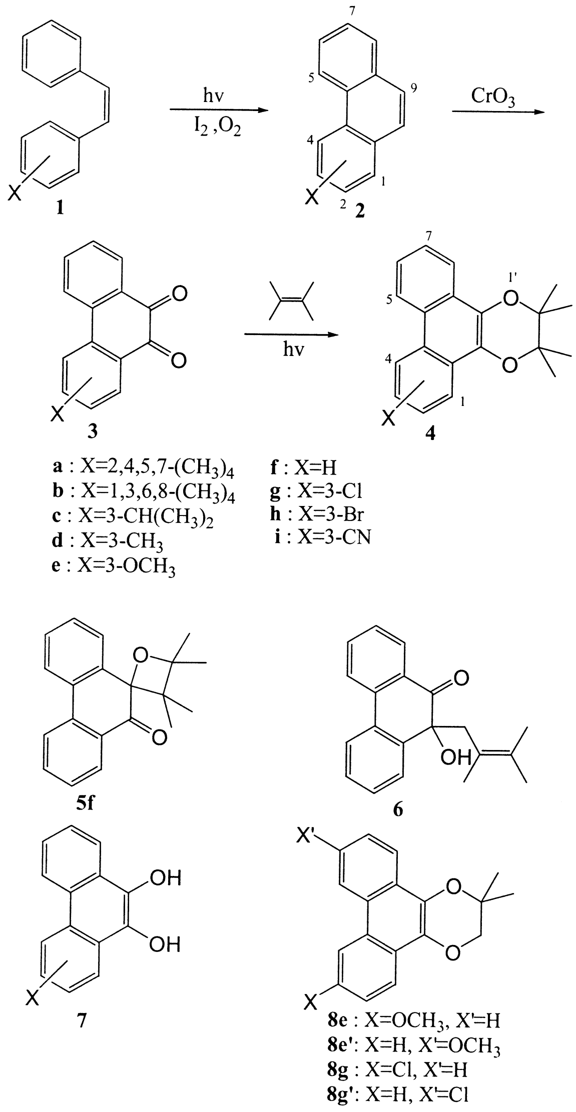
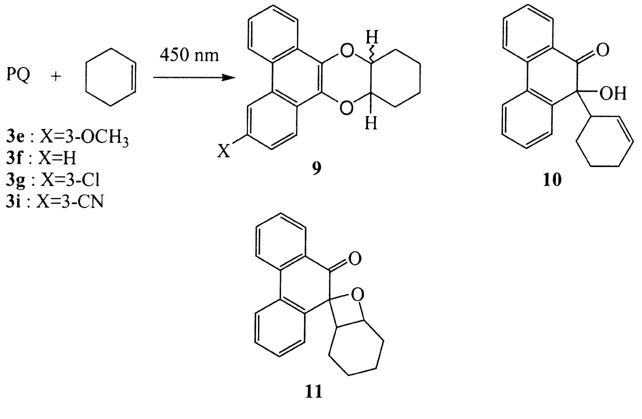
1010-6030/01/$ – see front matter © 2001 Published by Elsevier Science B.V.
PII: S1010-6030(00)00402-0



Scheme 1.



Scheme 2.

gan MAT TSQ-46C spectrometer, high resolution mass spectra with a JEOL JMS-HX110 spectrometer, UV–VIS spectra with a Perkin-Elmer 555, emission spectra with a Perkin-Elmer LS-5, and ^{1}H NMR spectra with either a EM-390 at 90 MHz, Bruker AM-300 WB FT or AM-200 WB FT spectrophotometer. Gas chromatographic analysis was carried out with a HITACHI 163 instrument equipped with either a SE-30 or OV-1 column at the injection and column temperatures of 240 and 220°C using tetracosane as the internal standard.

2.1.2. *Preparation of substituted PQ's*

The required phenanthrenes were prepared by light promoted oxidative cyclization of appropriately substituted 1,2-diphenylethenes in the presence of iodine in cyclohexane according to the literature method [18]. For example, a cyclohexane solution (100 ml) of 4′-methyl-1,2-diphenylethene (0.5 g) and iodine (0.05 mol%) was irradiated in Hanovia apparatus under oxygen purging with a 450 W medium pressure mercury lamp with water cooling. The photolysate was monitored with GC during irradiation, and the reaction was stopped after 100 h. The crude product was passed through an alumina column to give 3-methylphenanthrene [18,19].

Without further purification and identification these phenanthrenes were oxidized in glacial acetic acid [19,20]. The above 3-methylphenanthrene (0.27 g) and chromic trioxide (0.54 g) in glacial acetic acid (200 ml) was stirred at 80°C for 1 h and then at 110°C for 30 min. The cold solution was diluted with water (50 ml) and extracted with chloroform. The residue from the extracts was chromatographed on silica gel using a hexane–ethyl acetate mixture (20:1) as an eluent to give 3-methylphenanthroquinone. Other substituted PQ's were also prepared in the same method to give yields >75%, and as high as 90% in some cases [21].

2.2. *PQ preparative photocycloadditions*

2.2.1. *To TME*

A benzene solution containing a PQ (0.01 M) and TME (0.1 M) was distributed in 10–12 ml portions each among several Pyrex test tubes. The tubes were sealed with septa and purged with nitrogen. These tubes were placed around a Hanovia irradiator and photolyzed until the typical yellow color was bleached or until TLC analysis showed the disappearance of the quinone spot, the duration of which was generally 2–4 h. Alternatively, the solution was charged directly in a Hanovia vessel and irradiated for about 2 h under constant nitrogen purging. In either types of irradiation, the photolysate was evaporated to give a crude product that was adsorbed on a silica gel column and eluted with hexane to give dioxenes that were readily crystallized from ether.

2,4,5,7-Tetramethyl-1′,4′-dioxene (**4a**) was obtained in 66%; mp 184°C; ^{1}H NMR (300 MHz CDCl$_3$, TMS): δ = 1.33 (s, 6H), 1.45 (s, 6H), 2.50 (s, 6H), 2.51 (s, 6H), 7.10 (s, 2H), 7.22 (s, 2H); MS *m/z* (%): 348 (56) [M^+], 236 (100), 84 (28); IR (KBr): 1627, 1607, 1282, 1253, 1224, 1148 cm^{-1}; $C_{24}H_{28}O_2$: calc. C 82.72, H 8.10; found C 82.83, H 8.17.

1,3,6,8-Tetramethyl-1′,4′-dioxene (**4b**) was obtained in 60%; mp 186°C; ^{1}H NMR (300 MHz $CDCl_3$, TMS): $\delta =$ 1.41 (s, 12H), 2.51 (s, 6H), 2.90 (s, 6H), 7.13 (s, 2H), 8.27 (s, 2H); MS *m/z* (%): 348 (52) [M^+], 236 (100), 84 (30); IR (KBr): 1610, 1263, 1224, 1153 cm^{-1}; $C_{24}H_{28}O_2$: calc. C 82.72, H 8.10; found C 82.83, H 8.20.

3-Isopropyl-1′,4′-dioxene (**4c**) was obtained in 67%; mp 84–86°C; ^{1}H NMR (300 MHz $CDCl_3$, TMS): $\delta = 1.40$ (d, $J = 6.9$ Hz, 6H), 1.44 (s, 12H), 3.16 (septet, $J = 6.9$ Hz, 1H), 7.49–7.61 (m, 3H), 8.14 (d, $J = 8.4$ Hz, 1H), 8.19 (dd, $J = 8.0$, 1.4 Hz, 1H), 8.44 (d, $J = 0.8$ Hz, 1H), 8.63 (d, $J = 7.5$ Hz, 1H); MS *m/z* (%): 334 (46) [M^+], 252 (63), 84 (100); IR (KBr): 1629, 1607, 1245, 1228, 1145 cm^{-1}; $C_{23}H_{26}O_2$: calc. C 82.60, H 7.84; found C 83.00, H 8.10.

3-Methyl-1′,4′-dioxene (**4d**) was obtained in 55%; mp 114–115°C; ^{1}H NMR (300 MHz $CDCl_3$, TMS): $\delta = 1.42$ (s, 12H), 2.58 (s, 3H), 7.39 (d, $J = 8.2$ Hz, 1H), 7.52 (m, 1H), 8.06 (d, $J = 8.3$ Hz, 1H), 8.17 (d, $J = 7.8$ Hz, 1H), 8.37 (s, 1H), 8.58 (d, $J = 8.0$ Hz, 1H); MS *m/z* (%): 306 (8) [M^+], 224 (100), 84 (74); IR (KBr) 1627, 1606, 1285, 1244, 1227, 1152 cm^{-1}; $C_{21}H_{22}O_2$: calc. C 82.32, H 7.24; found C 82.25, H 7.21.

3-Methoxy-1′,4′-dioxene (**4e**) was obtained in 56%; mp ~46°C; ^{1}H NMR (300 MHz $CDCl_3$, TMS): $\delta = 1.42$ (s, 12H), 3.90 (s, 3H), 7.21 (dd, $J = 9.0$, 2.4 Hz, 1H), 7.46 (t, $J = 8.2$ Hz, 1H), 7.54 (t, $J = 8.1$ Hz, 1H), 7.97 (d, $J = 2.4$ Hz, 1H), 8.12 (d, $J = 9.0$ Hz, 1H), 8.18 (d, $J = 8.1$ Hz, 1H), 8.49 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR (75 MHz $CDCl_3$, TMS): $\delta = 22.7$, 55.4, 77.2, 77.5, 104.3, 116.2, 120.7, 121.2, 122.2, 122.4, 123.9, 125.8, 126.5, 127.3, 127.8, 129.7, 131.6, 157.1; MS *m/z* (%): 322 (63) [M^+], 239 (100), 84 (45); IR (neat) 1630, 1603, 1264, 1237, 1145 cm^{-1}; $C_{21}H_{22}O_3$: calc. C 78.23, H 6.88; found C 78.15, H 7.30.

1′,4′-Dioxene (**4f**) was obtained in 69%; mp 134°C; ^{1}H NMR (300 MHz $CDCl_3$, TMS): $\delta = 1.44$ (s, 12H), 7.55 (m, 4H), 8.19 (dd, $J = 7.8$, 1.4 Hz, 2H), 8.60 (d, $J = 7.8$ Hz, 2H); MS *m/z* (%): 292 (40) [M^+], 210 (99), 84 (100); IR (KBr) 1625, 1602, 1287, 1249, 1229, 1146 cm^{-1}; $C_{20}H_{20}O_2$: calc. C 82.16, H 6.89; found C 82.32, H 7.18.

3-Chloro-1′,4′-dioxene (**4g**) was obtained in 67%; mp ~55°C; ^{1}H NMR (300 MHz d_6-acetone): $\delta = 1.45$ (s, 12H), 7.54–7.66 (m, 3H), 8.13–8.18 (m, 2H), 8.69–8.72 (m, 2H); MS *m/z* 326 (62) [M^+], 84 (100); IR (neat) 1627, 1598, 1281, 1242, 1228, 1146 cm^{-1}; $C_{20}H_{19}O_2Cl$: calc. C 73.50, H 5.86; found C 73.51, H 6.05.

3-Bromo-1′,4′-dioxene (**4h**) was obtained in 70%; mp ~60°C; ^{1}H NMR (300 MHz d_6-acetone): $\delta = 1.44$ (s, 12H), 7.54–7.66 (m, 2H), 7.71 (dd, $J = 8.7$, 2.0 Hz, 1H), 8.06 (dd, $J = 9.0$, 3.0 Hz, 1H), 8.15 (m, 1H), 8.71 (d, $J = 8.1$ Hz, 1H), 8.86 (s, 1H); MS *m/z* (%): 372 (42) [M^+], 84 (100); IR (neat) 1628, 1605, 1281, 1227, 1146 cm^{-1}; $C_{20}H_{19}O_2Br$: calc. C 64.70, H 5.16; found C 64.64, H 5.43.

2.2.2. *To isobutene*

The solutions of **3e** and **3g** in benzene (0.004 M) were sealed in Pyrex tubes with rubber septa and purged with nitrogen. Approximately 0.1 g of isobutene was condensed through a needle. The solution was irradiated with the same light source until the color was discharged. The crude product from each PQ's was chromatographed to give the dioxene fraction which contained a 1:1 mixture of two photoproducts (**8e**–**8e**′ or **8g**–**8g**′). The H NMR spectra of either mixtures showed two sharp singlets of a same intensity at 4.1 ppm with 2.4 Hz separation, and only one strong singlet at 1.45 ppm for the C-methyl groups.

2.2.3. *To cyclohexene*

A solution of **3f** (375 mg, 1.8 mmol) and cyclohexene in benzene (180 ml) was sealed under nitrogen in a Pyrex tube (40 cm × 2 cm), which was irradiated in a Rayonet reactor with 4500 Å lamps for 15 min when the typical yellow color disappeared. The photolysate was evaporated, and the crude product was passed through a silica gel column using hexane–ethyl acetate as the eluent to give a mixture of *cis/trans* **9f** (28%, ratio 10/1), hydroxyketone **10** (47%), keto-oxetane **11** (12%) and residual **3f** in the order of elution (6,7,12). Repeated chromatograph of the **9f** fraction afforded small amounts of the *cis* and *trans* **9f** isomers. In separate experiment, a solution similar to above but in cyclohexane was irradiated for 15 min to give **9f** (44%), **10** (28%) and residual **3f** (12%) without the presence of keto-oxetane **11**. The spectral data are listed below.

Cis-1′,4′-dioxene (*cis*-**9f**): ^{1}H NMR (300 MHz $CDCl_3$): $\delta = 1.52$ (m, 2H), 1.80 (m, 4H), 2.11 (m, 2H), 4.47 (d, $J = 7.8$ Hz, 2H), 7.51–7.63 (m, 4H), 8.15 (d, $J = 8.0$ Hz, 2H), 8.60 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (75 MHz $CDCl_3$): $\delta = 21.6$, 28.0, 72.4, 120.7, 122.4, 124.5, 126.4, 126.5, 126.6, 131.7; MS (70 eV, EI): *e/m* (%): 290 (100) [M^+], 210 (68), 180 (76), 152 (21); HRMS ($C_{20}H_{18}O_2$): calc. 290.1307; found 290.1326.

Trans-1′,4′-dioxene (*trans*-**9f**): ^{1}H NMR (300 MHz $CDCl_3$): $\delta =$ 1.45–1.66 (m, 4H), 1.92 (d, $J = 8.8$ Hz, 2H), 2.42 (d, $J = 12.7$ Hz, 2H), 3.93 (m, 2H), 7.49–7.59 (m, 4H), 8.18 (d, $J = 8.1$ HZ, 2H), 8.58 (d, $J = 7.9$ Hz, 2H); MS (70 eV, EI): *e/m* (%): 290 (100) [M^+], 210 (65), 180 (74), 152 (37); HRMS ($C_{20}H_{18}O_2$): calc. 290.1307; found 290.1302.

Hydroxyketone (**10**): including two diastereomers: ^{1}H NMR (200 MHz $CDCl_3$): $\delta =$ 1.26–1.82 (m, 6H), 2.43 (m, 1H), 5.26(d, $J = 10.1$ Hz, 0.6H), 5.55 (d, $J = 10.1$ Hz, 0.4H), 5.72 (m, 1H), 7.28–7.37 (m, 3H), 7.54–7.85 (m, 5H); ^{13}C NMR (75 MHz $CDCl_3$): $\delta = 21.4$, 21.6, 23.5, 24.3, 24.4, 24.7, 45.8, 46.4, 81.4, 81.6, 122.8, 122.9, 123.9, 124.2, 124.4, 124.6, 126.6, 126.7, 126.9, 127.1, 127.3, 127.8, 127.9, 128.2, 128.3, 128.9, 129.0, 129.5, 130.1, 131.3, 133.8, 134.7, 134.5, 137.5, 137.6, 138.6, 139.3, 204.1, 204.2. MS (FAB) *e/m* (%): 291 (24) [$M^+ + $H], 290 (5) [$M^+$], 210 (55), 82 (100); IR (KBr): 1693 cm^{-1} (C=O), 3483 cm^{-1} (O–H).

Keto-oxetane (**11**): ^{1}H NMR (200 MHz $CDCl_3$): δ = 0.84–1.10 (m, 1H), 1.10–1.26 (m, 2H), 1.43–1.67 (m, 4H), 2.00–2.05 (m, 1H), 2.93 (dd, J = 15.8, 8.5 Hz, 1H), 5.14–5.22 (m, 1H), 7.33–7.44 (m, 3H), 7.60 (td, J = 7.6, 1.5 Hz, 1H), 7.73–7.78 (m, 1H), 7.82 (d, J = 7.6 Hz, 1H), 7.88–7.92 (m, 1H), 7.97 (dd, J = 7.6, 1.3 Hz, 1H). MS (FAB) *e/m* (%): 291 (100) [$M^+ + H$], 290 (37) [M^+], 209 (87), 181 (36); IR (KBr): 1702 cm^{-1} (C=O), 1600 cm^{-1} (aryl).

In a separate series of reactions, benzene solutions containing cyclohexene (0.1 M) and a PQ (**3e**, **3f**, **3g** or **3i**) placed in respective test tubes were irradiated at 450 nm for 10–25 min in the same manner as above. Each solution was worked up separately as stated above to give the dioxene fraction. The H NMR spectra of each samples showed well separated signals of the two methine protons at the ring fusion for *cis* **9** and *trans* **9,** the integration of these signals were used to calculate the ratio of the *cis/trans* isomers in each dioxenes (see Table 3). As for **9i**, the amount of *trans* **9i** was too small to be accurately integrated, this ratio was set as the limit of >20/1.

Cis/trans-3-methoxy-1′,4′-dioxene (*cis/trans*-**9e**): ^{1}H NMR (300 MHz $CDCl_3$): δ = 1.47–1.52 (m, 2H), 1.75–1.79 (m, 4H), 2.08 (m, 2H), 2.40 (d, J = 12.2 Hz), 3.90 (m, 0.14H) 3.98 (s, 3H), 4.43 (d, J = 6.2 Hz, 0.86H), 7.22 (dd, J = 9.0, 2.1 Hz, 1H), 7.48 (td, J = 8.2, 1.2 Hz, 1H), 7.56 (td, J = 7.9, 1.0 Hz, 1H), 7.97 (d, J = 2.1 Hz, 1H), 8.09 (d, J = 9.0 Hz, 1H), 8.15 (d, J = 7.9 Hz, 1H), 8.49 (d, J = 8.2 Hz, 1H).

Cis/trans-3-chloro-1′,4′-dioxene (*cis/trans*-**9g**): ^{1}H NMR (300 MHz $CDCl_3$): δ = 1.49–1.53 (m, 2H), 1.78–1.81 (m, 4H), 2.04–2.12 (m, 2H), 2.41 (d, J = 10.7 Hz), 3.92 (m, 0.12H), 4.45 (d, J = 6.6 Hz, 0.88H), 7.50 (dd, J = 8.8, 1.9 Hz, 1H), 7.52 (m, 1H), 7.59 (td, J = 8.0, 1.4 Hz, 1H), 8.10 (d, J = 8.8 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.48 (d, J = 8.3 Hz, 1H), 8.52 (d, J = 1.9 Hz, 1H).

Cis/trans-3-cyano-1′,4′-dioxene (*cis/trans*-**9i**): ^{1}H NMR (300 MHz $CDCl_3$): δ = 1.52 (m, 2H), 1.73–1.85 (m, 4H), 2.03–2.09 (m, 2H), 2.41 (m), 3.93 (m, *ca.* 0.05H), 4.46–4.52 (m, 0.95H), 7.59–7.65 (m, 2H), 7.73 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.3 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.88 (s, 1H).

2.2.4. The quantum yields of dioxene formations

2.2.4.1. Under 450 nm irradiation and by the ferrous oxalate actinometry. The sample preparation in this section was performed in a dark room under red light. A benzene solution (10 ml) containing PQ (**3f**, 0.01 M) and TME (0.1 M) was placed in a Pyrex test tube (11 mm × 100 mm) and sealed under nitrogen with a rubber septum. Separately, an aqueous ferrous oxalate (0.01 M) solution (10 ml) was also sealed under nitrogen in a similar test tube. Two tubes were placed diagonally in a “merry-go-round” of a Rayonet photochemical reactor and irradiated with 450 nm lamps (RPR 4500 Å) for 1 min while they were rotated. The latter solution was diluted with a standard phenanthroline solution [22] (10 ml) to record the UV absorption curve; the intensity at 510 nm was used to calculate the concentration of the Fe^{2+}-phenanthroline complex. The mole equivalent of the consumed Fe^{2+} ion in the solution was used to calculate the quantum input to each tubes on the basis of the reported quantum yield of 1.11 for the Fe^{2+} ion transformation [22]. Under the conditions, the photon absorbed by the actinometric solution (i.e. the quantum input) was determined to be 7.48×10^{-6} mole. A half of the PQ photolysate was evaporated to give the crude product, the NMR spectrum of which showed dioxene **4f** as the only detectable product. The photolysate was diluted with benzene by the factor of 10 to record the UV spectrum, and the optical density at 373 nm was used to calculate the concentration of **4f**. This was in turn used to calculate the mole equivalent of **4f** produced; this was divided by the quantum input to afford the quantum yield of **4f** as 0.96 under the irradiation conditions.

Several solutions of PQ and dioxene **4f** of known concentrations were prepared to record their UV absorption curves. The optical densities at several wavelengths were plotted against the solution concentration to give a straight line with correlation of 0.999. This correlation line was used to read the concentration of **4f** in photolysates in the related experiments.

2.2.4.2. Quantum yield determinations through H NMR. Benzene solutions (10 ml each) containing a fixed PQ concentration (0.01 M) and increasing concentrations of TME (0.04–0.50 M) were placed in separate test tubes and purged with nitrogen through a septum seal. These tubes were rotated in the “merry-go-round” and irradiated with 450 nm lamps for 1 min. Each photolysate was separately evaporated, and the crude product taken up in $CDCl_3$ (1 ml) was examined with H NMR. The ratio of the integrated intensity of the dioxene methyl signal (12H) and of the C1–C10 protons (2H) of PQ was used to calculate the ratio of **4f**/**3f**; these two intensities were large and sensitive to changes in a low conversion region. This ratio was used, in turn, to calculate the yield of **4f** at the conversion of **3f** in the range of 10–15%. The yields were used to calculate the quantum yields using $\Phi = 0.96$ at [TME] = 0.1 M as the secondary actinometry (see the experiment above). At the TME concentration of 0.04, 0.08, 0.10, 0.30 and 0.50 M, the quantum yield of dioxene **4f** was 0.75, 0.90, 0.96, 0.98 and 0.91, respectively (see Table 1).

2.2.4.3. Quantum yields of other dioxenes in chloroform. Chloroform solutions of PQ (**3f**) and 3-chloro-PQ (**3g**, 0.01 M each) in the presence of TME (0.1 M) in separate test tubes were irradiated under the same conditions using the same secondary actinometry as above. The products were quantitatively determined by H NMR spectroscopy as described above. The quantum yield of **4f** and **4g** were calculated to be 0.70 and 0.71 (see Table 1).

Table 1
The quantum yields of the photocycloaddition of PQ (0.01 M) with TME[a]

[TME]	PQ's					
	2,4,5,7-$(CH_3)_4$ (**3a**)	1,3,6,8-$(CH_3)_4$ (**3b**)	3-$CH(CH_3)_2$ (**3c**)	3-OCH_3 (**3e**)	H (**3f**)	3-Cl[a] (**3g**)
0.01	0.058	–	0.38	–	–	0.57
0.02	0.13	0.12	0.48	0.50	0.46	0.64
0.03	0.19	–	0.51	0.58	–	0.78
0.04	0.22	0.26	0.53	–	0.62 (0.75)[b]	–
0.06	–	–	–	–	0.65	–
0.08	0.45	0.32	0.68	0.79	0.70 (0.90)[b]	0.94
0.10	–	–	–	–	0.78 (0.96)[b]	(0.71)[c]

[a] Solutions in benzene were irradiated with RPR 3000 Å except the photocycloaddition of 3-chloro-PQ for which chloroform was used, see Section 2 for the detail.

[b] The benzene solutions were irradiated at 450 nm: for comparison, similar irradiation in chloroform gave $\Phi = 0.70$ at [TME] = 0.1 M.

[c] Irradiated at 450 nm.

2.2.4.4. Under 300 nm irradiation. Two benzene solutions containing PQ (0.01 M) and TME (0.1 M) were separately placed in each quartz tubes; one was sealed under nitrogen and the other under air, and both were irradiated in a "merry-go-round" at 300 nm (by Rayonet RPR 3000 Å) for 1 min. Simultaneously, a stilbene actinometry solution was also placed together for irradiation. This actinometer [23] was established based on the quantitative isomerization of *trans*- to *cis*-stilbene in a low conversion region of about 10% [24], and possessed quantum yields of 0.45, 0.45, 0.44 and 0.38 at [*trans*-stilbene] = 0.01, 0.05, 0.10 and 0.25 M, respectively, the % yields of stilbene isomers were determined by GC. For both PQ photolysates, the dioxene yields were determined by H NMR to be 15±0.3% which afforded the quantum yields $\Phi = 0.78$ and 0.77, respectively.

The quantum yield of the photocycloaddition of various PQ's (0.01 M) in benzene to TME at increasing concentrations (0.01–0.10 M) were determined by the same process as described above using the quantum yield ($\Phi = 0.78$) of **4f** under the conditions as the actinometer. Owing to the low solubility, 3-chloro-PQ (**3g**) was dissolved in chloroform for the determination. The calculated quantum yields are listed in Table 1.

2.2.5. Absorption–emission spectra and lifetime measurements

For absorption and emission spectral measurements, cyclohexane solutions containing PQ (about 10^{-5} M) and TME in various concentrations were prepared. When the preparation of the solution was made under room light conditions, the recorded spectra showed new peaks rapidly and poor reproducibility depending on elapsed times. Hence, all solution preparations for spectral and quantum yield measurements were carried out in a dark room under red light. The variation of fluorescence and absorption spectra caused by time elapses are shown in Fig. 2a and b.

A solution of a PQ (about 10^{-4} M) in a mixture of ethanol–ethyl ether (1:1) formed a transparent glass at 70 K. Phosphorescence spectra were recorded with excitation of the glass at 313 nm. The phosphorescence decay curve monitored at the peak was analyzed to give a good first order kinetic which gave the triplet lifetime shown in Table 2. For some dioxenes **4**, their phosphorescence spectra and lifetimes were also recorded by excitation at 320 nm as shown in Table 2.

PQ's in carbon tetrachloride (10^{-3}–10^{-4} M) gave phosphorescence spectra on excitation at 405 nm to give maximums at about 585 and 640 nm, such as that shown in Fig. 3. The phosphorescence intensity was reduced in the presence of increasing TME concentrations from 10^{-4}–10^{-5} M. Analysis of the major peak intensity according to the Stern-Volmer equation gave $k_q\tau$ values that ranged 45 000–60 000. The triplet lifetime of PQ **3f** under the same conditions in carbon tetrachloride was determined by the analysis of the decay curve monitored at the major peak to be 62 μs.

2.2.5.1. Quenching of the PQ photoreaction. To four test tubes containing benzene solution of PQ (0.01 M) and TME (0.1 M), 0.1 M of 1,3-cyclohexadiene, *trans*-stilbene and anthracene was added separately to three tubes, the fourth served as the blank. These samples sealed under nitrogen were irradiated in the "merry-go-round" for 1 min at 450 nm where upon the yellow color in the fourth tube turned paler. The four samples were worked up for H NMR determinations of **3f** and **4f** as above. The fourth sample gave **4f** (80%). The first sample gave both PQ and **4f** in 40%. The second

Table 2
Phosphorescence data of **3** and **4** in solid solution

Substituents	PQ **3**[a]		Dioxene **4**[b]	
	λ_{max} (nm)	τ (ms)	λ_{max} (nm)	τ (ms)
2,4,5,7-$(CH_3)_4$ (**a**)	521	12	–	–
3-$CH(CH_3)_2$ (**c**)	–	–	485	53
H (**f**)	561	7.1	485	54
3-Cl (**g**)	554	10	498	35
3-Br (**h**)	554	7.5	498	7.1

[a] Taken in EtOH:Et_2O = 1:1 at 77 K.

[b] Taken in EtOH at 77 K.

Table 3
Reduction potentials and calculated ΔG^{*} for triplet state reactions[a]

PQ's	E_{red} (V)	E_T (V)	ΔG^{b}	*Cis/trans*[c]
3-$CH(CH_3)_2$ (**3c**)	−0.662	2.16	0.080	–
3-OCH_3 (**3e**)	−0.602	2.19	0.010	6/1 (**9e**)
H (**3f**)	−0.660	2.16	0.086	10/1 (**9f**)
3-Cl (**3g**)	−0.566	2.16	−0.010	7/1 (**9g**)
3-Br (**3h**)	−0.474	2.16	−0.090	–

[a] The conditions of cyclic voltammetry is described in the Section 2.

[b] Calculated from Rehm-Weller equation using the oxidative potential of TME 1.21 V (see [16]).

[c] The ratio of cycloaddition of 3-CN PQ **9i** to cyclohexene was placed as the limiting value $> 20/1$.

sample gave **4f** (40%) and small amount of *trans*-stilbene. The third sample gave PQ (80%) and **4f** (20%).

2.2.5.2. Redox potential determinations. The cyclic voltammetry of PQ's was determined in dimethylformamide or acetonitrile using tetrabutylammonium perchlorate as the electrolyte with an electrochemical analyzer BAS-100, which equipped a AgCl/Ag reference electrode, a glassy carbon working electrode, and a platinum auxiliary electrode. The scanning conditions were 100 mV/sec in the range of 0.0–1.0 V. The representative cyclovoltammograms were shown to be reversible. The reduction potential was corrected with respect to the standard calomel electrode by adding 0.05 V (Table 3).

3. Result

Phenanthroquinone (**3f**, PQ), the parent member, is commercially available, but other substituted phenanthroquinones (**3**, PQ's) were prepared by two step reactions starting from substituted stilbenes **1**. First of all, stilbenes **1** were oxidatively photocyclized [18] to give substituted phenanthrenes **2** by prolonged irradiation (Scheme 1). This was followed by chromic trioxide oxidation of **2** to give PQ's **3**, the yields of these could be raised to >90% after a set of suitable conditions was found [20,21]. These PQ's showed a deep yellow color and similar absorption spectra exhibiting peaks in the vicinity at $\lambda_{\max}$ 257, 314, 420 and 510 nm, the variation of substituents in **3a**–**3i** did not alter the absorption wavelength and intensity significantly, indicating the lack of electronic perturbations by the substituents at the 3-position.

Except 3-chloro, 3-bromo and 3-cyano PQ's (**3g–3i**), other PQ's in Scheme 1 were readily soluble in benzene; chloroform was a good solvent for all of these PQ's to make up to 0.01 M solutions. We re-confirmed [6–11] that benzene is the best solvent for the reaction since other solvents, particularly good H-atom donating solvent (such as methanol), caused reduction to give 9,10-dihydroxyphenanthrene **7**. The initial investigation used Hanovia lamp and allied photocells but later Rayonet Irradiator was found to be more convenient when this became available. Irradiation of a benzene solution of a PQ's **3** (0.01 M) and TME (0.1 M) under nitrogen in Hanovia apparatus through a Pyrex filter was followed by TLC monitor to show the slow consumption of PQ and gave the corresponding substituted derivatives of 2′,2′,3′,3′-tetramethyl-1′,4′-dioxa-1′,2′,3′,4′-tetrahydrotriphenylene **4** which was abbreviated as dioxenes. The irradiation generally took about 4 h, but did not require 20 or more hours as reported previously [9,16]. The reported long irradiation time could arise from the use of TLC for end-point analysis wherein the PQ trace persisted from the re-oxidation of **7** by the air leading to the erroneous judgment; the photoreaction is indeed unusually efficient as shown below. The progress of the reaction also could be followed by GC analysis, but generally the discharge of the dark yellow color indicated a near consumption of PQ's. For **3g–3i**, a suspension in benzene solution was used that gave satisfactory preparative results since the corresponding products **4g–4i** were readily soluble in benzene. Dioxenes **4** were readily isolated in good yields by simple chromatography. Minor quantities of other products were also formed (but not isolated) as shown by small peaks in GC of these photolysates. They were most likely the Paterno-Büchi type [25] 1,2-adduct **5** and reductive addition products **6** as shown by GC–MS examinations and on the basis of the reported reaction pattern [4–11], the former oxetanes **5** was known to be photolabile [6–8] to give the starting materials and **4** (see below).

All dioxenes **4** showed pertinent H NMR, IR and MS data and elemental analysis in agreement with the proposed structure, except some anomalies mentioned below. Dioxene **4a** exhibited two singlets (1.45 and 1.33 ppm) for the four chemically identical methyl groups of the dioxene ring in contrast to the isomeric dioxene **4b** (and other dioxenes) which showed only one singlet for the four corresponding methyl groups. The magnetic non-equivalence of the former must be caused by a locked distortion of the phenanthrene ring in **4a** from the steric crowding at the angular 4,5-dimethyl groups, that hold the dioxene ring in a rigid, semi-chair conformation. This forced **4a** to assume the distinct axial and equatorial methyl groups in the dioxene ring. The consequence of molecular distortion in **4a** also accidentally induced near magnetic equivalence of the four aromatic methyl groups that revealed themselves as two closely placed singlets at 2.50 and 2.51 ppm. The non-coplanarity of **3a** has been demonstrated by X-ray crystallography [26], that provided a rationale for the conclusions arrived above for **4a**. It was noteworthy other dioxenes **4c–4i** also show only one signal for the four methyl groups in the dioxene ring in spite of the presence of two chemically non-equivalent methyl pairs (except **4f**) due to a substituent at a benzene ring (see below).

The photocycloaddition of 3-methoxy-PQ **3e** and 3-chloro-PQ **3g** with isobutene gave a pair of isomeric adducts in each case (**8e–8e′** and **8g–8g′**) that could not be separated on various attempts. The NMR spectra of both

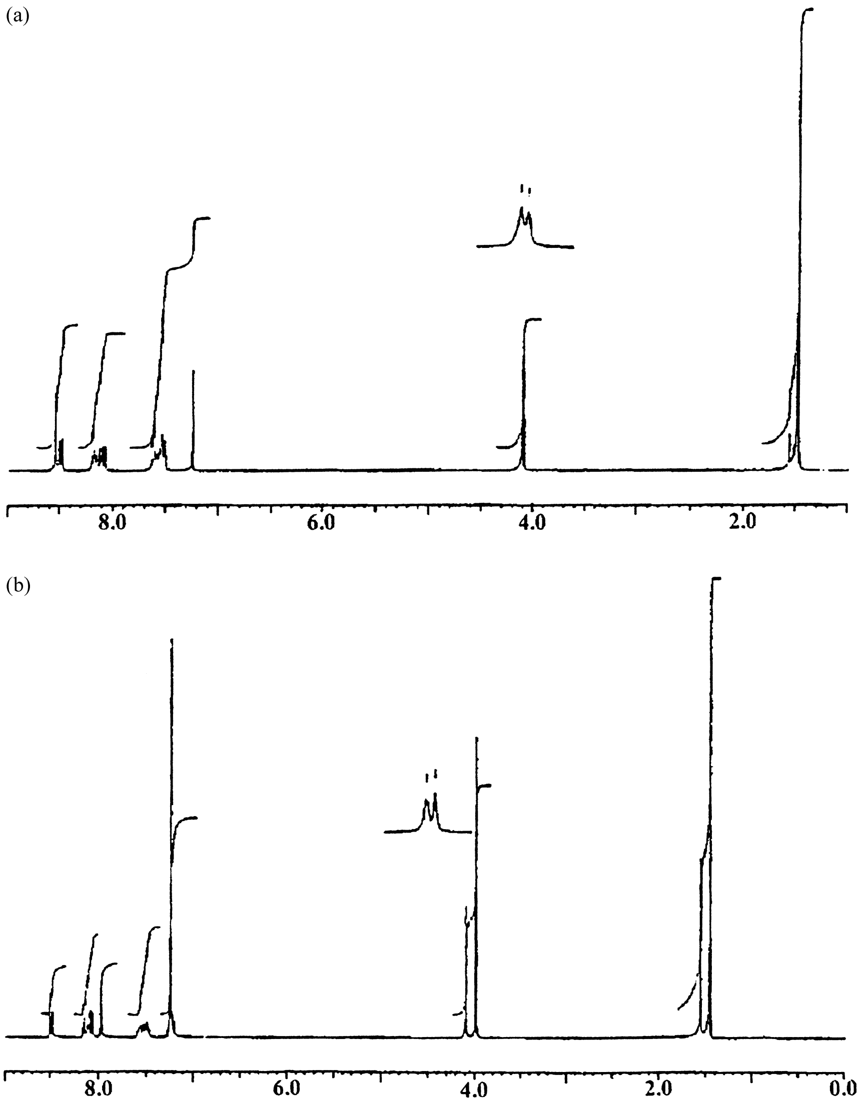


Fig. 1. The H NMR spectra of the 1:1 mixtures of **8e–8e′** and **8g–8g′**.

mixtures showed two closely placed singlets for the methylene group (–OCH2–) at ca. 4.1 ppm with a peak separation of only 2.5 Hz. Both mixtures also showed one singlet each for the two *geminal*-dimethyl groups in respective pairs. The former mixture showed only one methyl singlet at 4.2 ppm for two types of the methoxy group **8e′**–**8e** (Fig. 1). The lack of spectral response to the variation of 3-substituents shown here and above suggested that the substituents transmitted minimum magnetic and electronic perturbations to the dioxene ring, likewise, the asymmetry of dioxene ring had no effect on the methoxy chemical shift. The photocycloaddition of PQ with TME at 0.10 M was somewhat retarded under purging of oxygen to give a slightly smaller amount of dioxene **4f**. However, at [TME] $\leq$ 0.01 M, while the reaction was more severely retarded the addition product **4f** was not completely quenched (compare with the quantum yield determination below). In the later case, a small amount of a mixture of oxidation products, diphenic acid and its derivatives were also formed as shown by GC–MS analysis. PQ was mainly photoreduced to 9,10-dihydroxyphenanthrene **7** not only in methanol but also, unexpectedly, in acetic acid though less efficiently. In benzene, photoreaction of PQ in the presence of 4-pentenoic acid was slow and gave diol **7** which was gradually re-oxidized during the product isolation in the air to PQ. The small fractions of minor products in the photolysate were examined by GC–MS, but showed no product incorporating the carboxylic acid. Also in the presence of fumaronitrile, no addition occurred under prolonged irradiation.

In cyclohexane, PQ showed no fluorescence except feeble peaks at 378 and 399 nm that were shown to arise from a trace amount of diol **7** as an impurity in the sample. In the presence of TME, the solution showed increasing intensity for these two peaks as well as an additional third one at 423 nm as the exposure time increased in a fluorescence spectrophotometer (Fig. 2a). These three fluorescence peaks

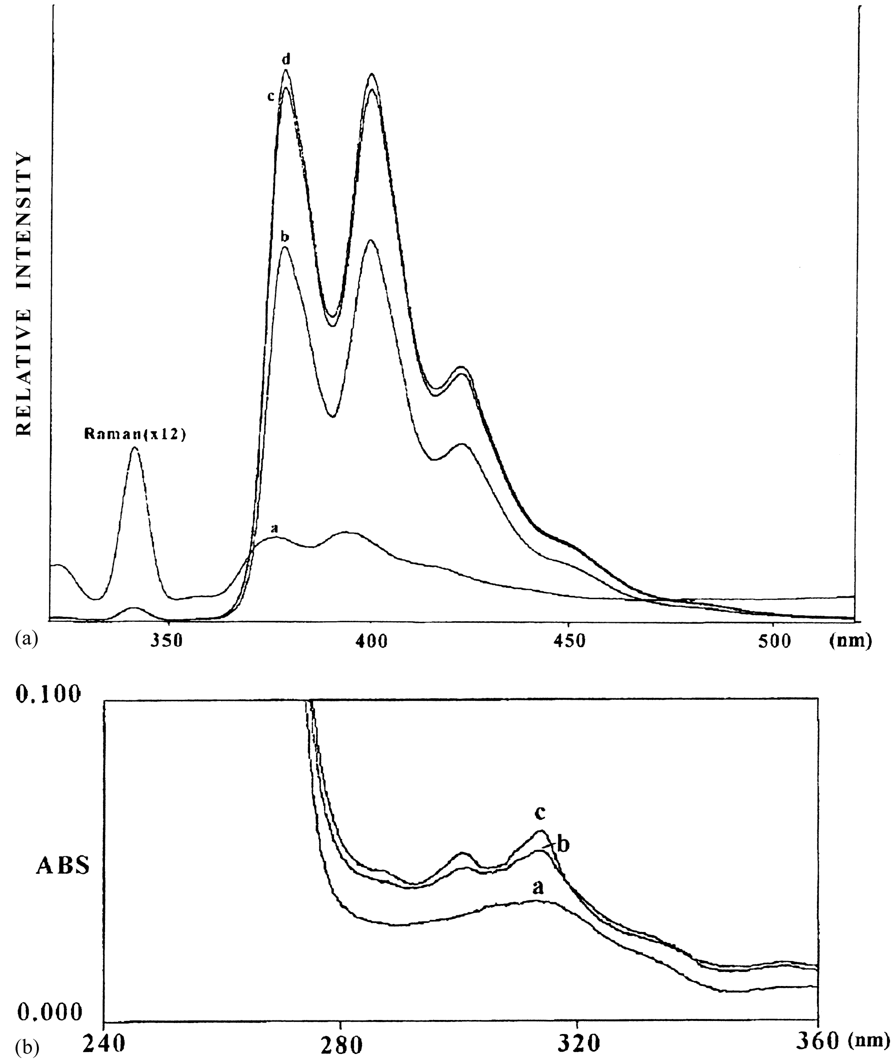


Fig. 2. (a) Fluorescence spectra of [PQ] 10^{-5} M in cyclohexane with λ_{exc} at 310 nm (curve a) immediately after preparation (curve b) in the presence of [TME] 0.1 M after 1 min exposure in the fluorimeter, (curve c) and (curve d) those exposed continuously for 20 and 30 min, respectively; (b) UV–VIS absorption spectra of [PQ] 10^{-5} M and [TME] 0.1 M in cyclohexane (curve a) immediately after the preparation in dark, and (curve b) and (curve c) after exposure to room light for 20 and 40 min, respectively.

were due to the dioxene **4f** as established by comparison with an authentic spectrum. A dilute PQ solution (10^{-5} M) in cyclohexane taken in UV–VIS spectrophotometer showed weak absorption peaks around 320 nm, but in the presence of TME the absorption intensity in this region increased enormously due to the formation of **4f**. Indeed, a freshly prepared solution when exposed to room light gradually develops these absorption peaks (Fig. 2b), the solution of which also exhibited the fluorescence spectrum of **4f**. While the monitor of fluorescence or absorption in fluid solution was frustrated by the extraordinarily rapid photoreaction, phosphorescence spectra of several PQ's in solid solution at 77 K were recorded readily. Their triplet lifetimes were also obtained by monitoring the decay profiles at the absorption peak (in the region of 520–560 nm) to be 7–12 ms (Table 2). Using the same procedure, the phosphorescence maximums and lifetimes of some dioxenes **4** were also determined to be much longer as listed in Table 2.

PQ's showed phosphorescence emission in carbon tetrachloride at room temperature with λ_{max} near 585 nm (e.g. Fig. 3), which was located far from those shown by dioxenes **4**. In the presence of increasing concentration of [TME] = $10^{-5} - 10^{-4}$ M, the phosphorescence intensity of various PQ's decreased progressively. The intensity ratio at the peak wavelength (I_0/I) plotted against [TME] according to the Stern-Volmer equation showed good linear plots that passed through the vicinity of $I_0/I = 1$ at [TME] = 0 M. The quenching constants $k_q\tau$, obtained from the slopes, were large, in the range of 20 000–68 000 reflecting a long lifetime of triplet excited PQ's and efficient quenching by TME. Using a time resolved phosphorescence monitor, the PQ triplet state lifetime [21] could be determined under the same con-

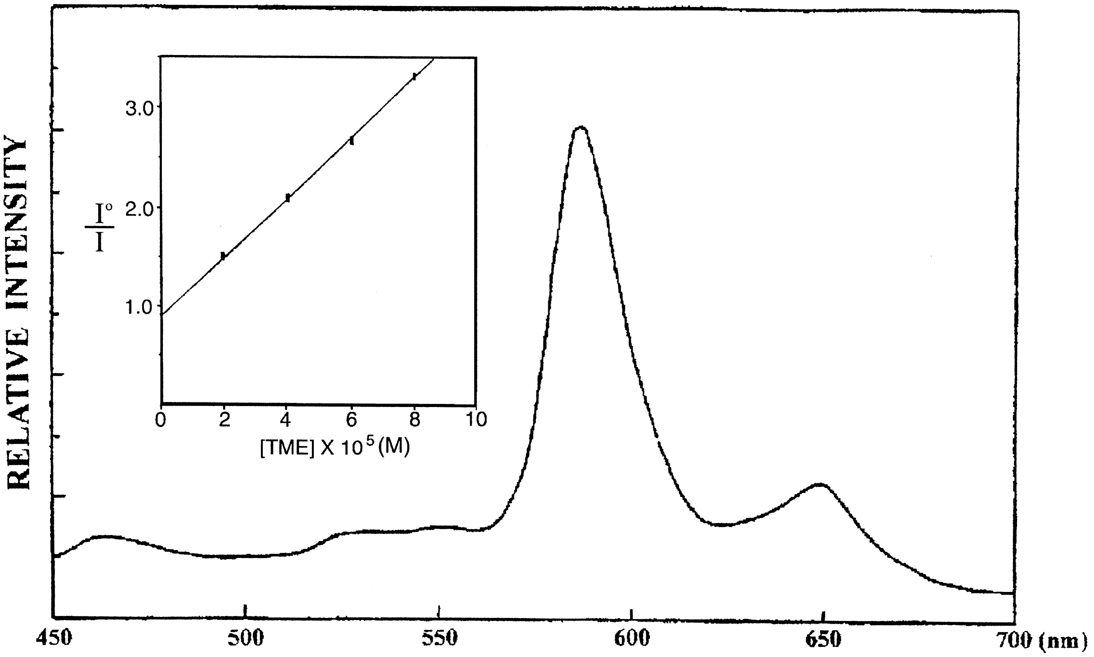


Fig. 3. The phosphorescence spectrum of PQ (**3f**) in carbon tetrachloride solution at the room temperature, the inset shows the Stern-Volmer plot of the intensity quenching by TME.

ditions (i.e. in carbon tetrachloride and at room temperature) on the basis of a decay trace recorded at the peak wavelength. The lifetimes were much shorter than those determined in solid solutions and varied greatly (e.g. 60 ± 25 μs) depending on the purity and cleanliness of each experiments owing to long triplet lifetimes that are sensitive to impurity quenching. Thus, accurate measurements of the quenching efficiency by phosphorimetry were not possible. If we assume an average lifetime of triplet PQ's in preparative runs to be 10 μs, shorter owing to impurity quenching in preparative runs, the calculated k_q is lower than but close to the diffusion controlled bimolecular rate constants, $10^{-10}\,M^{-1}\,s^{-1}$.

The photocycloaddition of TME to PQ on exposure to room light suggested the extraordinarily efficient reaction at 400–500 nm n–*π excitation. Abnormally high quantum yields recorded in the initial phase of this work [21] must have been caused by exposure during solution preparations. Subsequently, quantum yields of the dioxene formation were determined under dark room conditions using a Rayonet irradiator. Benzene solutions of PQ (0.01 M) and TME (0.1 M) sealed under nitrogen and air, respectively, were irradiated at 300 nm (RPR 3000A lamps) in the presence of the actinometer based on the isomerization of *trans*-stilbene to the *cis*-isomer. This actinometry was developed on the basis of the original photoreaction [23,24]. The product yields were calculated (to be 15.3%) from the NMR integration of the 12 methyl-hydrogen atoms in the dioxene ring of **4f** and two *peri*-hydrogen of **3f**. The quantum yields of **4f** under nitrogen and air were 0.78 and 0.77, respectively. Subsequently, the solution containing PQ (**3f**, 0.01 M) and TME (0.1 M) in benzene under nitrogen was used as the secondary actinometer ($\Phi_4 = 0.78$) to determine the dioxene quantum yields under various TME concentrations, ranging 0.01–0.10 M. Various PQ's at 0.01 M in benzene (except 3-chloro-PQ **4f** which was in chloroform) were used for quantum yield determinations at the conversion of about 10% as determined from relevant NMR intensities (see Table 1).

Irradiation of a benzene solution of PQ (0.01 M) and TME (0.1 M) for 5 min at 450 nm gave only **4f** with an conversion of about 65%, similar irradiation but with 300 nm gave a crude product showing the same NMR spectrum with only 40% conversion. The efficient photocycloaddition by 450 nm irradiation was further confirmed by the quantum yield of dioxene formations using the ferrous oxalate actinometry [22] taking care to work under dark conditions. A benzene solution of PQ (**3f**, 0.01 M) and TME (0.1 M) kept under nitrogen was irradiated at 450 nm for 1 min in a "merry-go-round" to give 15.7% conversion; the yield of dioxane **4f** and the **3f** conversion were determined by predetermined plots of UV optical densities against concentrations. The quantum yield of **4f** was 0.96 as determined against the ferrous oxalate actinometric solution. This solution ([TME] = 0.10 M, $\Phi_4 = 0.96$) was now used as the secondary actinometry to determine the **4f** quantum yield under the similar conditions in the presence of [TME] 0.04, 0.08, 0.10, 0.30 and 0.50 M, that gave the quantum yield ranging 0.75–0.98 as shown in Table 1. These data demonstrated the trend of the quantum yield variation to approach unit as [TME] reaching to 0.1 M. Separately, the formation quantum yield in chloroform for dioxenes **4f** and **4g** from **3f** and **3g** at [TME] = 0.1 M was determined to be 0.70 and 0.71, respectively.

Similar solution containing PQ (0.01 M) and TME (0.1 M) and irradiation conditions at 450 nm were used for quenching experiments. In the presence of 0.1 M of 1,3-cyclohexadiene, *trans*-stilbene and anthracene in each sample, the yield of **4f** was reduced to 50, 50 and 25%, respectively, with respect to that of the unquenched photoreaction after short irradiation. In the presence of 1,3-cyclohexadiene, small amounts of new products were also formed but not investigated. The photoreaction of PQ with *trans*-stilbene was slow and no new product was found in the quenching photolysis.

In view of reported long irradiation times in previous reports, the PQ photocycloaddition with cyclohexene in benzene was re-investigated with 450 nm irradiation. In this reaction 0.01 M PQ solution in the presence of cyclohexene (0.1 M) was almost bleached in 15 min to give dioxene **9f** (28%, a *cis/trans* mixture), hydroxyketone **10** (47%), keto-oxetane **11** (12%), this result was comparable to those reported [6–11] except that the present result produced **11**. The same solution, when photolyzed with 300 nm irradiation, gave a more complex product pattern but no keto-oxetane **11** in agreement with previous report [6–11]. It has been demonstrated that allied keto-oxetanes could be photolyzed at >300 nm to give products which include dioxenes and starting materials [7,8]. In contrast to these results, it was also reported [15,16] that norbornenes and other bridged bicyclic olefins photolytically reacted with PQ to give exclusively the corresponding keto-oxetanes that were relatively photostable. The hydorxyketone **10** was relatively stable and survived >300 nm irradiation. We believe that the excited state of **10** dissipates energy by a reversible attack on the double bond since no pathway is available to stabilize the diradical intermediate. Using the same conditions, photoreaction of PQ's (**3e–3g** and **3i**) with cyclohexene were also run to afford crude dioxene fractions, the *cis/trans* ratio of which were examined by the H NMR integration of the methine proton signals (at the vicinity of 3.9 and 4.4 ppm) to give 6/1, 10/1, 7/1 and >20/1, respectively. The assignment of the *cis/trans*-configuration was based on the chemical shift difference in accordance to the literature [7–9]. In the integration of sample **9i** obtained from 3-cyano-PQ **3i**, the yield of *trans*-**9i** was too small to give accurate integration, and the *cis/trans* ratio was estimated to be >20/1.

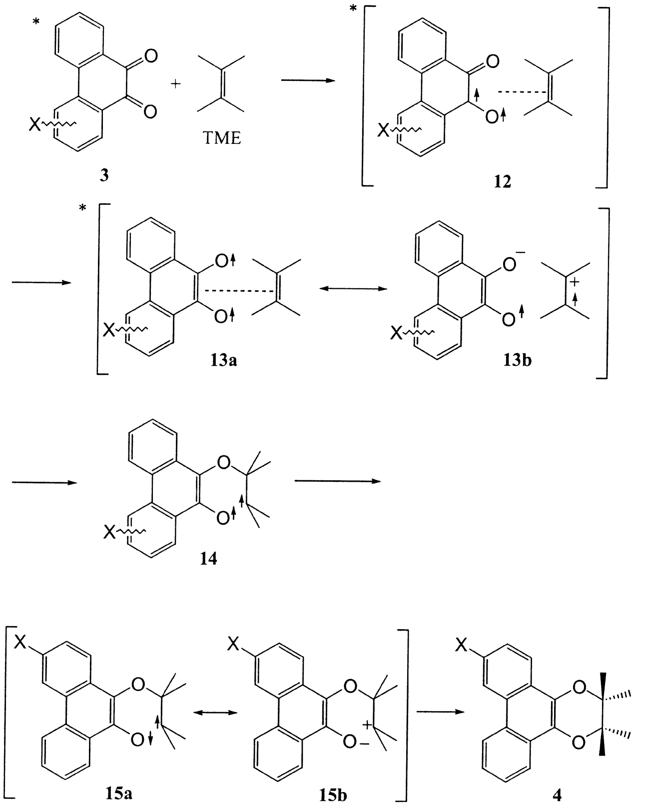
It became critical to know the role of electron transfer in the photocycloaddition [27,28] that required the reduction potential for PQ's. These PQ's in solution showed a near-reversible reduction trace in cyclic voltammetry. The reduction potentials of PQ's determined from peak to peak potentials, corrected for the standard electrodes, are listed in Table 3.

4. Discussion

While the photocycloaddition of 1,2-quinones with olefines is a general reaction, these data have demonstrated that of PQ's with TME is unique among others with the following characteristics. Firstly, it is remarkably efficient and clean to give dioxenes **4** and can be induced by visible light (450–500 nm) with the limiting quantum yield of unity. Direct demonstrations of the formation of dioxene **4f** by room light and also in spectrometers indeed reveal this reaction to have a rarely observed efficiency. Secondly, the reaction is initiated from the long-lived PQ triplet excited state and only weakly susceptible to substituent effects. The triplet excited state reaction is amply supported by product quenching experiments by oxygen and other triplet quenchers and, also by the phosphorescence intensity reduction by TME. The latter can not be analyzed accurately by means of the Stern-Volmer equation owing to PQ's possessing a long triplet state lifetime and its sensitivity to the experimental conditions. Even without accuracy, the high reactivity is shown by the reduction of the phosphorescence intensity by TME concentrations as low as 10^{-5}–10^{-4} M that is translated into the Stern-Volmer quenching constants in the order of 50 000, extraordinarily large k_{SV}. Thirdly, this and the failure of oxygen to reduce the chemical and quantum yields of **4f** under those measuring conditions squarely place the interaction of the triple PQ state with TME as fast as that with oxygen, that is, at the diffusion controlled rate constant. Finally, in view of the high quantum efficiency, it is logical to conclude that *every collision of the reactants must lead to the* ***4f*** *formation*.

The most useful new discovery in the present study is that the 450 nm (or visible light) excitation does give higher and cleaner (chemical as well as quantum) yields of dioxene **4** than 300 nm excitation does. This must arise in part from the retardation by the build up of **4f** due to its strong absorption in the 300–350 nm region. However, the comparison is reliable and valid since the conversions are low. As we have shown that dioxenes **4** are stable to 300 nm irradiation, lower yields by 300 nm irradiation must arise from reasons other than the secondary photolysis of **4** itself, that reasons could be complex owing to many absorbing species and sensitization therefrom within the photolysate. One speculation is that an primary addition intermediate, such as **13** and/or **14** in Scheme 3, may revert to the starting materials, this is more likely to occur from 300 nm excitation owing to substantial residual vibration energy. The effects of substituent at the 3-position in PQ in the photocycloaddition to TME turned out to be small and random on quantum yields, triplet properties, and quenching rate constants. This probably shows the domination of quinone triplet excited state in dictating the reactivity, which also involves the aromatization to a phenanthrene. However, the tetramethyl substituted PQ's **3a** and **3b** give distinctly lower quantum yields of photocycloadducts **4a** and **4b** than others, the reason of which remains un-accountable.

The photocycloaddition of triplet PQ with cyclohexene is just as efficient but gave hydroxyketone **9** as the major and keto-oxetane **10** as the minor products. The former **9** is derived from hydrogen abstraction from four relatively reactive secondary allylic hydrogens. The formation of latter Paterno-Büchi type products, keto-oxetane **10**, is apparently



Scheme 3.

dependent on the structural factor of olefins since TME scarcely give the corresponding compound. The exclusive formation of this adduct type in good yields from norbornenes and allied bridged olefins with triplet PQ is indeed noteworthy (**16**) and has been explained by steric factors.

It has been agreed that PQ's react from the lowest triplet excited state on the basis of the similarity to benzophenone (and related aromatic ketone) photoreations, that are generally known to react from the n–$^{*}\pi$ triplet state [29–31]. The absorption peak of PQ at 510 nm (ε, 100) has all the characteristics of n–$^{*}\pi$ transition, thus the efficient reaction from 450 nm excitation must occur from this triplet excited state. The quenching of the **4f** formation by typical triplet quenchers, such as 1,3-cyclohexadiene, *trans*-stilbene, and anthracene, and also in oxygen saturated solution provide supporting evidence for the triplet state reaction. Secondly, the PQ phosphorescence quenching by TME directly demonstrates the triplet reaction though the quenching data were not precise. The reduction of the phosphorescence intensity at $[\mathrm{TME}] = 10^{-5}$ M can not come from the singlet quenching since that would require the singlet lifetime of >10 μs on the assumption of a diffusion controlled quenching. In fact PQ must have a singlet state lifetime shorter than picosecond as it does not give fluorescence as shown in Fig. 2a. The phosphorescence lifetime of about 10 ms in solid solution and about 100 μs in liquid solution shown by PQ are typical of triplet state carbonyl compounds [32]. It should be noted that the triplet lifetime of 3-bromo-PQ (**3h**) is not shorter than those of other PQ's (see Table 2), indicating the lack of internal heavy atom effects, this supports the n–$^{*}\pi$ transition of the PQ's excited state. In contrast, the corresponding effect in dioxenes is clearly shown by shorter lifetimes of **4g** (3-chloro) and even shorter one of **4h** (3-bromo), this indicates that the dioxene triplet state possesses a π–$^{*}\pi$ transition which can respond to spin-orbit couplings [33,34].

The basic pattern of the photocycloaddition mechanism is outlined in Scheme 3. This is essentially an extension of the Paterno-Büchi reaction [25] which has been generally agreed as a stepwise radical reaction as shown by **12** → **13** → **14**, except that some favoring the intervention of an exciplex intermediate [30,31] but other advocating a diradical formation directly [29] from the triplet excited state. We consider that a critical question is the electronic structure of diradical intermediates **13** and **15**, i.e. the degree of the charge transfer contribution (**13b** and **15b**) prior to the respective bond formations. Such electron transfer must create dipole interaction that should contribute to maintain a certain degree of stereochemical retention and of regioselectivity [28]. In the present discussion, CT and exciplex formation in **13** refer to the same driving force since both broadly lead to similar stereochemical consequence. In the literature, PQ photocycloadditions to simple *cis* and *trans* acyclic olefins has been shown to give the same dioxene isomeric ratio [6–11], this is compelling evidence for the lack of CT in these reactions. However, partial stereochemical retention is known in other photocycloadditions with 1,2-quinones of better electron acceptors reacting with good electron donating stilbenes [12–14]. The free energy of photoinduced electron transfer for some PQ's from TME calculated by the Rehm-Weller equation [27] gives small and random variations in the 0 V region (Table 3). While quantitative comparison can not be done owing to different solvents, these calculation can be used as a guide to show that there is only a small degree of the CT contribution in **13**, that scarcely show variations by the substituents. By extrapolation, a CT contribution in **15** can be regarded to be small also. The lack of a CT contribution in the PQ photoreaction is further supported. First, the total lack of regioselectivity in the photocycloaddition of 3-chloro-PQ **3g** and 3-methoxy-PQ **3e** to isobutene (Fig. 1) indicates that during the approach of reactants electron transfer (i.e., the contribution of **13b**) does not develop to any appreciable extent; it gives triplet 1,4-radical **14** directly. Secondly, in the photocycloaddition to cyclohexene, the ratio of *cis*-**9**/*trans*-**9** shows small changes without regularity for **9e** (3-methoxy), **9f** and **9g** (3-chloro), but definitely in favor of *cis*-**9i** for the case of 3-cyano PQ. *This pattern indicates that the contribution of the CT form* **15*b*** *is not significant until the strongly electron withdrawing 3-cyano group is in conjugation.* Finally, the lack of participation of the carboxylic acid group by an ionic mechanism in the PQ photoreaction with 4-pentenoic acid [35] or in acetic acid also indirectly support this conclusion of the poor CT contribution in the process.

Overall, these results confirm the previous proposal of a 1,6-diradical intermediate [3–11] and further add evidence for a weak CT contribution prior to and during cycloaddition [15,16]. Indeed, our results favor the model of a direct attack of ketone diradical rather than that of a triplet state exciplex [29]. The quantum yield of this photocycloaddition is extraordinary high reaching the limiting value of unity for **4f** and **4g** in benzene as shown in Table 1, for these two cases, obviously, every collisions of reactants lead to a successful dioxene formation. Coupled with the fact that the triplet state diradical of PQ's is long-lived, all these factors contribute to non-selective cycloaddition in term of regio- and stereo-chemical consequences. This PQ photoreaction is notably different from that of acyclic aromatic 1,2-diketones, for example, benzil does not undergo photocycloaddition with olefins [36,37]. The discrepancy must arise from dipole orientation of the vicinaldiketone group in excited states. It should be added that subtle conformational differences have been inferred as a source of divergent reactivity in 1,4-diradicals generated in photoinduced intramolecular hydrogen abstraction of ketones [17].

Acknowledgements

The authors wish to thank National Science Foundation of Taiwan, Taipei for generous financial supports of this project. And the help of a triplet lifetime measurement from Professor T. S. Fang is greatly appreciated. YLC also wish to thank Natural Science and Engineering Council of Canada, Ottawa for the financial support of operating grants.

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