2- and 4-Methoxyphenanthrene. A solution of 630 mg (3 mmol) of *trans-m*-methoxystilbene and 38 mg (0.15 mmol) of iodine in 300 ml of cyclohexane was irradiated for 5.5 hr to give a mixture of 4-methoxyphenanthrene (shorter glc retention time) and 2-methoxyphenanthrene (longer glc retention time) in the ratio of 42/58. The crude products were chromatographed on alumina with ligroin as eluent. Material obtained from several early fractions was recrystallized from petroleum ether (30–40°) and then from aqueous ethanol to give 4-methoxyphenanthrene, mp 67.8–68.7° (lit.[42] mp 68°). Material from later fractions was recrystallized from 95% ethanol to give 2-methoxyphenanthrene, mp 97.4–98.2° (lit.[43] mp 99°).

trans-m-**Fluorostilbene.** The Grignard reaction of *m*-fluorobenzylmagnesium chloride with benzaldehyde followed by dehydration of the resulting carbinol with aqueous sulfuric acid gave *trans-m*-fluorostilbene. Purification by sublimation and recrystallization from methanol gave material with mp 73.0–73.7° (lit.[44] mp 74–75°).

2- and 4-Fluorophenanthrene. A solution of 1.39 g (7 mmol) of *trans-m*-fluorostilbene and 89 mg (0.35 mmol) of iodine in 400 ml of cyclohexane was irradiated for 16 hr. The product composition was shown by glc analysis to be 41% 4-fluorophenanthrene (shorter retention time) and 59% 2-fluorophenanthrene (longer retention time). These two components were separated by chromatography on alumina with petroleum ether (30–40°) as eluent. The first-eluted material was recrystallized from methanol to give 4-fluorophenanthrene, mp 41.0–42.6° (lit.[45] mp 47°). The material obtained from further elution of the column was recrystallized from methanol to give 2-fluorophenanthrene, mp 102.6–104.6° (lit.[45] mp 104–105°).

Acknowledgment. We are grateful to the Alfred P. Sloan Foundation for supporting this work.

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[42] R. Pschorr and B. Jaeckel, *Chem. Ber.*, 33, 1826 (1900).

[43] R. Pschorr, *ibid.*, 34, 3998 (1901).

[44] W. J. Linn, *J. Amer. Chem. Soc.*, 87, 3665 (1965).

[45] P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, 4486 (1955).

Photochemical Reactions of Diketones. V.[1] Reaction of Phenanthrenequinone and Benzene[2]

Mordecai B. Rubin* and Ziva Neuwirth-Weiss

Contribution from the Department of Chemistry,
Technion, Israel Institute of Technology, Haifa, Israel.
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Abstract: The photochemical reaction (degassed) of phenanthrenequinone (PQ) and benzene affords principally a 1:1 adduct, the monophenyl ether (**8**) of 9,10-dihydroxyphenanthrene, as well as biphenyl and 9,10-dihydroxyphenanthrene (PQH_2). The wavelength independent (313–436 nm) quantum yield for disappearance of PQ is 0.13. Deuterium isotope effects using hexadeuteriobenzene (C_6D_6) or C_6D_6–C_6H_6 mixtures show that biphenyl is formed *via* addition of phenyl radicals to benzene. The formation of **8** was not affected but iodobenzene replaced biphenyl as a product when irradiation was performed at 404 nm in the presence of iodine. The reaction of PQ with chlorobenzene afforded the mono-*p*-chlorophenyl ether of PQH_2 and at least three dichlorobiphenyls. Quenching with anthracene afforded a linear Stern–Vollmer plot. It is suggested that triplet PQ may abstract hydrogen from benzene to form PQH· and phenyl radicals or add reversibly to benzene to give diradical **10**. The adduct **8** may be formed either from **10** or a geminate pair of PQH· and Ph· radicals after spin inversion but before diffusion from the solvent cage in which they form.

Photochemical reactions[3] of 9,10-phenanthrenequinone (PQ) in the absence of oxygen can be divided into two main classes: (1) photocycloaddition with olefins proceeding *via* a diradical **1** which may cyclize to dioxene **2** or keto oxetane **3** or rearrange to the new radical **4** which cyclizes to dioxole **5**; (2) hydrogen abstraction from a wide variety of H donors which results in formation of semiquinone radical PQH· and the donor derived radical D·; subsequent radical combinations lead to 1:1 adducts **6** or **7** while disproportionation of two PQH· radicals results in formation of 9,10-dihydroxyphenanthrene (PQH_2) with regeneration of PQ. Dimerization or other reactions of the radical D· may also be observed. Both classes of PQ photoreactions have been shown to proceed *via* the same excited state which is accepted[3] to be the n,π^* triplet ($E_T = 49$ kcal/mol).

In connection with our investigations of the scope of these reactions and as part of the search for a photochemically inert solvent for PQ, we were led to examine the photochemistry of PQ in benzene solution.[4] After this work was largely completed, a report[5] appeared describing the photoreduction of PQ in 2-propanol using benzene as solvent; flash photolysis of PQ in benzene resulted in observation of the triplet state of PQ (PQ^3) and of the semiquinone radical PQH·; the decay rates were 1×10^5 sec^{-1} for the triplet and 8.1×10^8 M^{-1} sec^{-1} for the semidione. Neither transient was observed in the presence of added anthracene; instead the anthracene triplet was observed.

Results

The changes observed in the uv spectrum of a degassed benzene solution 3.33×10^{-4} M in PQ upon irradiation at 436 nm are shown in Figure 1. Disappearance of the characteristic PQ absorption is accom-

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[1] For the previous paper in this series see M. B. Rubin and R. G. LaBarge, *J. Org. Chem.*, 31, 3283 (1966).

[2] A preliminary report of this work has appeared: M. B. Rubin and Z. Neuwirth-Weiss, *Chem. Commun.*, 1607 (1968).

[3] For reviews of quinone photochemistry see: J. M. Bruce, *Quart. Rev., Chem. Soc.*, 21, 405 (1967); M. B. Rubin, *Fortschr. Chem. Forschung*, 13, 251 (1969).

[4] The initial observation that dilute solutions of PQ in benzene are bleached by sunlight was made by R. A. Reith.

[5] P. A. Carapellucci, H. P. Wolf, and K. Weiss, *J. Amer. Chem. Soc.*, 91, 4635 (1969).

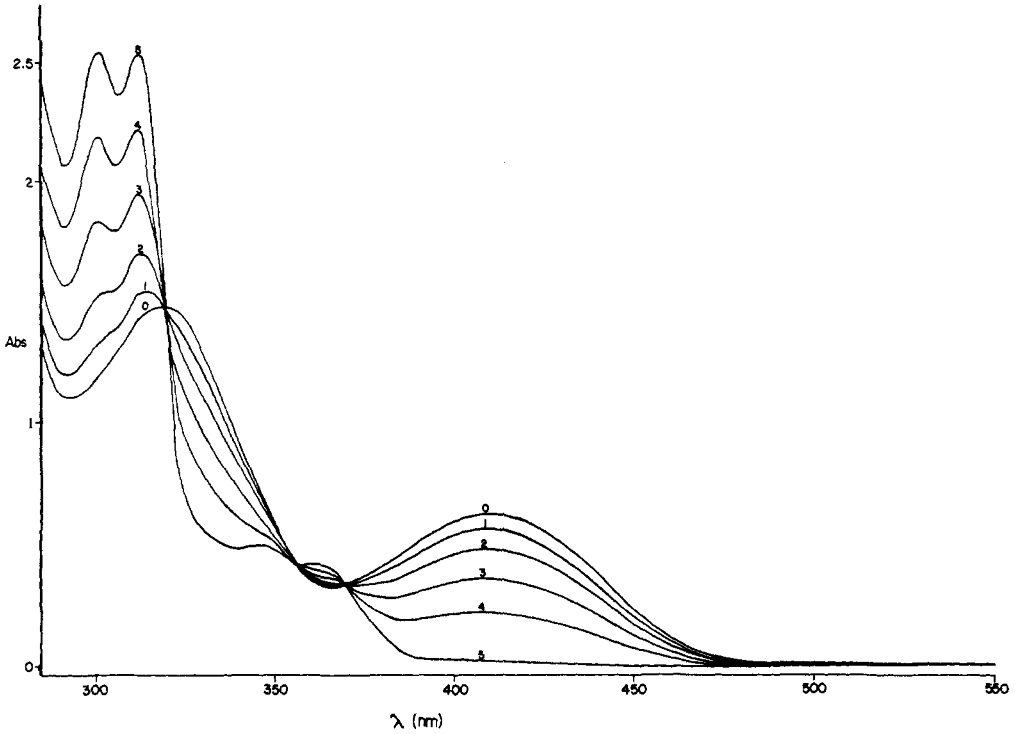
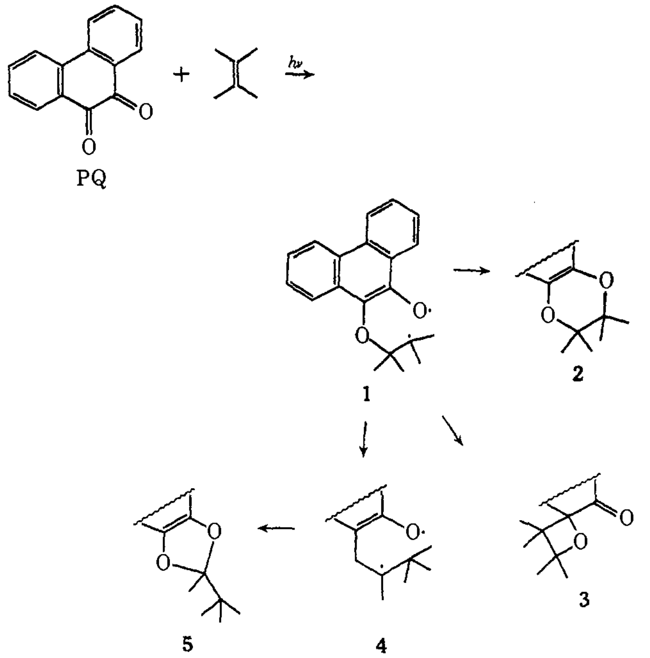
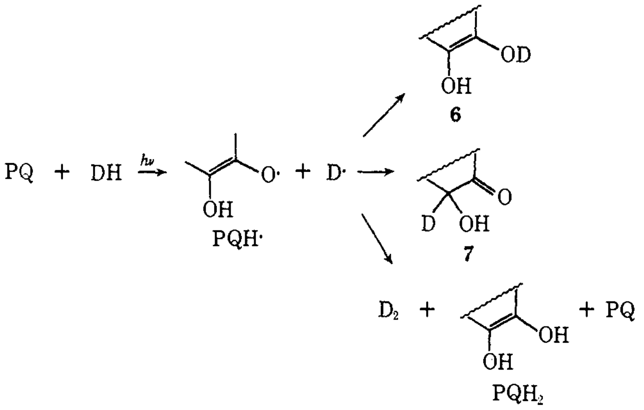


Figure 1. Spectra taken at intervals upon irradiation of PQ in degassed benzene solution at 436 nm.





panied by appearance of isosbestic points at 318, 354, and 368 nm and the final spectrum, after complete consumption of PQ, is characteristic of 9,10-dioxyphenanthrenes.[6] Admission of air to the cell resulted in slow regeneration of the PQ maximum at 410 nm until 22% of the original intensity was recovered; further standing did not result in any additional change. This behavior is characteristic[5] of PQH_2 although essentially complete recovery of the original PQ absorption would be expected if PQH_2 were the only product. The readily reproducible quantum yield[7] for PQ disappearance at 313, 366, 404, and 436 nm was 0.13; this value was also obtained in wet benzene at 436 nm. Lower, variable quantum yields were obtained when irradiations were performed without exclusion of oxygen;[8] gas chromatographic analysis indicated the presence of diphenic anhydride in the resulting reaction product.

Preparative scale reactions[9] were performed with 2.4×10^{-2} *M* PQ in benzene under nitrogen using a 450-W water-cooled immersion lamp surrounded by a glass filter eliminating radiation below 370 nm. After removal of most of the solvent and filtration of phenanthrenequinhydrone ($(PQH)_2$, 23%), chromatography on Florisil yielded biphenyl[10] (18%), the monophenyl

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[6] M. B. Rubin, *J. Org. Chem.*, 28, 1949 (1963).

[7] The value of 0.25 reported earlier[2] unfortunately included an arithmetical error.

[8] Photooxidation of PQ in a variety of solvents was first reported by A. Benrath and A. von Meyer, *Ber.*, 45, 2707 (1912), and recently reconfirmed by C. W. Bird, *Chem. Commun.*, 1537 (1968).

[9] At the higher concentration and greater light intensity required for preparative purposes, considerable phenanthrenequinhydrone was formed. This compound acted as an internal filter and prolonged irradiation time was required in order to achieve appreciable conversions.

[10] Some biphenyl was lost because of its volatility. On the basis of a blank run, it is estimated that the actual yield of biphenyl was about 25%.

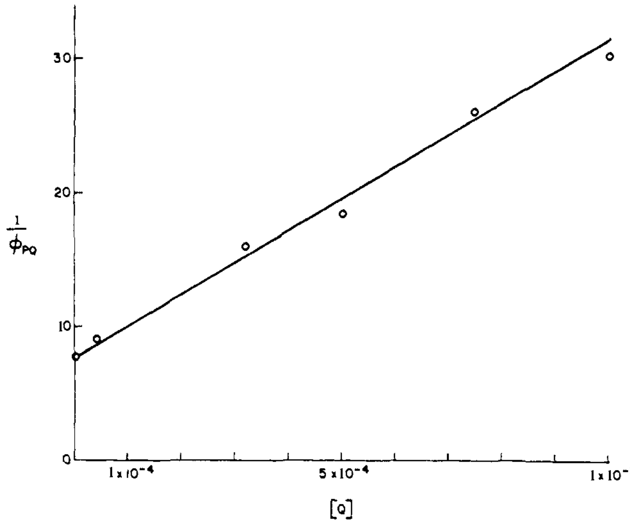
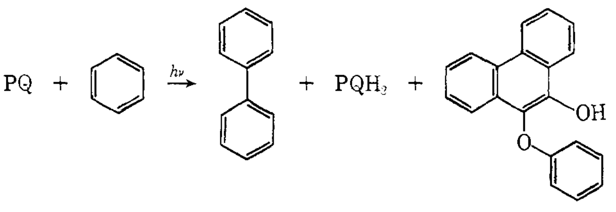


Figure 2. Plot of reciprocal of quantum yield for PQ disappearance *vs.* concentration (M) of added anthracene.

ether (**8**, 19%) of PQH_2, PQ (30%), and 9% of uncharacterized amorphous material. The melting point of **8** was identical with that reported by Goldschmidt, *et al.*,[11] in 1925 and the spectroscopic properties were all in agreement with the proposed structure.[12]



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Subsequent experiments were performed in order to clarify various aspects of mechanism of this reaction. First, it was shown that reaction in degassed solution was completely quenched by 10^{-2} M anthracene (E_T = 42 kcal/mol) and partially quenched at lower anthracene concentrations. A plot (Figure 2) of the reciprocal of quantum yield for PQ disappearance *vs.* anthracene concentration gave a good straight line with a least-squares slope of $2.2 \times 10^4\ M^{-1}$. Regeneration of 22% of the original PQ absorption was also observed when air was admitted to solutions after irradiation in the presence of anthracene. This constancy of composition indicates that all products are formed from the same excited state, presumably the n,π* triplet. For a simple mechanism involving unimolecular deactivation (k_d) of the triplet state of PQ, bimolecular reaction (k_r) of PQ^3 with benzene to afford intermediates which proceed to product and bimolecular, diffusion-controlled (k_q) quenching by anthracene, the steady-state approximation gives the expression

$$1/\phi = 1 + k_d/k_r[C_6H_6] + k_q[\text{anthracene}]/k_r[C_6H_6]$$

From the slope of the Stern–Vollmer plot (Figure 2) and assuming $k_q = 3.2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ for benzene at 25°, the calculated value is $k_r = 1.3 \times 10^4\ M^{-1}\ \text{sec}^{-1}$.

The reaction exhibited an isotope effect. Irradiation (436 nm) of PQ in degassed hexadeuteriobenzene (C_6D_6) proceeded with a quantum yield of 0.065, one-half the value observed in ordinary benzene. This result was not due to a photophysical effect as shown by analysis of the products obtained upon irradiation in C_6H_6–C_6D_6 mixtures. After washing out exchangeable (phenolic) deuterium, the ratio of undeuterated to pentadeuterated adduct, determined by mass spectroscopy, was consistent with an isotope effect $k_H/k_D = 2$ as observed in the quantum yield measurements.[13] The biphenyl fraction from such competition experiments was isolated by preparative scale gas chromatography and analyzed mass spectroscopically[16] for biphenyl, pentadeuteriobiphenyl, and decadeuteriobiphenyl. If there were no isotope effect in the formation of biphenyl, the ratio $C_{12}H_{10}$:$C_{12}H_5D_5$:$C_{12}D_{10}$ should be $1:2r:r^2$ where r represents the molar ratio C_6D_6:C_6H_6. The results presented in Table I clearly show that this is not the case and therefore a significant isotope effect is also involved in biphenyl formation. Detailed consideration of this point will be deferred to the Discussion section.

Table I. Relative Isotopic Distribution of Biphenyl from Irradiations[a] of PQ in Benzene–Benzene-d_6 Solvent

Molar ratio C_6D_6/C_6H_6	Biphenyls,[b] % $C_{12}H_{10}$	$C_{12}H_5D_5$	$C_{12}D_{10}$
0.49	72	27	
1.15	44	53	3
1.74	38	58	4
2.93	25	66	9

[a] Irradiation of 20 mg of PQ in *ca.* 2 ml of degassed solution at λ >390 nm. [b] Isotopic compositions determined mass spectroscopically.

A convenient minimum in the region of 400 nm in the absorption spectrum of iodine allowed iodine trapping experiments to be performed. It was shown that the quantum yield for PQ disappearance at 404 nm was not affected by the presence of an equimolar amount of iodine.[17] When such PQ–iodine mixtures were irradiated at 404 nm in degassed benzene on a semipreparative scale, it could be shown by gas chromatographic analysis that biphenyl was *not* formed but iodobenzene was obtained in a yield (20%) approximating that of biphenyl formed in the absence of iodine. Significantly, *the formation of adduct was not affected;* the yield of **8** was not appreciably different from that obtained in the absence of iodine.

The duality of mechanism suggested by the above results was also observed in reactions of PQ with chloro-

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(11) (a) S. Goldschmidt, A. Vogt, and M. A. Bredig, *Justus Liebigs Ann. Chem.*, **445**, 123 (1925). (b) This product has also been reported recently by C. Blomberg, H. H. Brootveld, T. H. Gerner, and F. Bickelhaupt, *J. Organometal. Chem.*, **24**, 549 (1970).

(12) The stoichiometry of this reaction and the close similarity of absorption spectra of PQH_2 and **8** account for the fact that isosbestic points can be observed even though a mixture of products is obtained.

(13) It might be noted that kinetic isotope effects of 2.7 were observed in photochemical hydrogen abstraction from benzhydrol[14] and 2-propanol.[15] These relatively low values are consistent either with a transition state occurring quite early or quite late on the reaction coordinate.

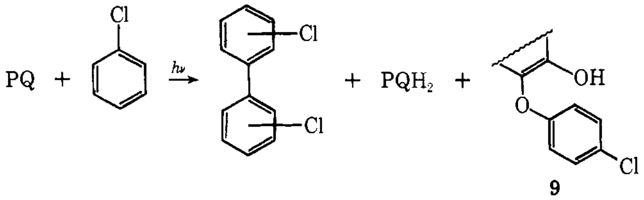
(14) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(15) W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

(16) We wish to acknowledge the cooperation of Dr. J. Deutsch in determining these spectra.

(17) (a) *Cf.* J. F. Garst and R. S. Cole, *Tetrahedron Lett.*, 679 (1963). (b) Irradiation of iodine in benzene at 404 nm did not result in any reaction; in particular, no iodobenzene was formed.

benzene. The quantum yield for PQ disappearance in degassed chlorobenzene solution was 0.03. Preparative scale irradiations afforded a single 1:1 adduct **9** (14%) and a mixture of dichlorobiphenyls. The adduct **9** was assigned the structure shown on the basis of its



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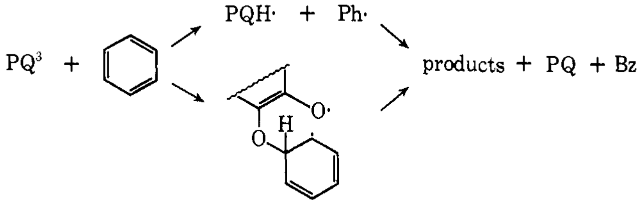
spectroscopic properties; in particular, the presence of a characteristic AB pattern in the nmr spectrum showed that reaction occurred at the position para to the chlorine. In contrast to the specificity observed in adduct formation, the nonpolar fraction of the reaction product showed three overlapping peaks upon gas chromatographic analysis; combined gas chromatography–mass spectrometry indicated that these three peaks were all dichlorobiphenyls. Unfortunately, we were unable to obtain samples of pure compounds because of the small amounts of mixture available and the difficulties involved in separation. It is thus not clear if the total number of dichlorobiphenyls formed is greater than three or not.

Discussion

The results of other investigators[3,5] and the anthracene quenching observed in the present work indicate that singlet PQ undergoes efficient intersystem crossing to the triplet which is the chemically reactive excited state. Since PQ^3 is known both to abstract hydrogen and to add to double bonds, both processes can *a priori* be considered in the case of benzene. H abstraction would give semiquinone (PQH·) and phenyl radicals (Ph·) which could then afford the observed products; alternatively, addition of PQ^3 to benzene would give the diradical **10** which may convert to adduct **8** simply by shift of a hydrogen atom. The conversion of **10** to PQH_2 and biphenyl is less obvious. The intermediates formed in either mechanism could, in principle, revert back to PQ plus benzene.



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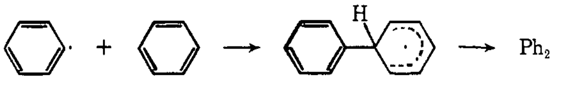
Both iodine trapping and chlorobenzene results suggest that, in fact, two different mechanisms originating from the same excited state are operative. It seems attractive to suggest that adduct **8** is formed *via* the diradical **10** while biphenyl and PQH_2 are products derived from PQH· and Ph· *via* H abstraction.[18] While **10** is not affected by iodine, the phenyl radicals are trapped as iodobenzene thus explaining the complete suppression of diphenyl formation concomitant with no effect on adduct formation. In order to explain the isotope effects observed on quantum yield and formation of **8**, it is necessary to assume that addition of PQ^3 to benzene to form **10** is "reversible;" if the subsequent hydrogen transfer step is slow and irreversible, an isotope effect will be observed.

If biphenyl formation involves phenyl radicals generated by H abstraction, occurrence of an isotope effect in its formation is hardly surprising. It should be noted that the distributions of biphenyl, pentadeuteriobiphenyl, and decadeuteriobiphenyl shown in Table I rule out the possibility that biphenyl is formed by coupling of two phenyl radicals since completely different distributions than observed would be expected. The observed distributions are consistent with a process[20] in which a phenyl radical adds to benzene to give radical **11**. Neglecting secondary isotope effects, the ratio of



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isotopically substituted biphenyls is given by

$$C_{12}H_{10}:C_{12}H_5D_5:C_{12}D_{10} = 1:r(a + 1/a):r^2/a^2$$

where r is the molar ratio $C_6D_6:C_6H_6$ and a is k_H/k_D. The value of k_H/k_D calculated from the results of Table I is 24 ± 4.

The following scheme can then be proposed.

$$PQ \xrightarrow{h\nu} PQ^1 \xrightarrow{\text{isc}} PQ^3 \quad \phi_{\text{isc}} \cong 1 \qquad (1)$$

$$PQ^3 \longrightarrow PQ \qquad (2)$$

$$PQ^3 + PhH \longrightarrow \mathbf{10} \qquad (3)$$

$$\mathbf{10} \longrightarrow PQ + PhH \qquad (4)$$

$$\mathbf{10} \longrightarrow \mathbf{8} \qquad (5)$$

$$PQ^3 + PhH \longrightarrow PQH\cdot + Ph\cdot \qquad (6)$$

$$2PQH\cdot \longrightarrow PQ + PQH_2 \qquad (7)$$

$$Ph\cdot + PhH \longrightarrow \mathbf{11} \qquad (8)$$

$$\mathbf{11} + PQ \longrightarrow Ph_2 + PQH\cdot \qquad (9)$$

The last step, conversion of **11** to biphenyl by hydrogen transfer to PQ is suggested in view of the relatively high concentration of PQ; alternative possibilities are hydrogen transfer from **11** to PQ^3 or to PQH. The deuterium isotope effect observed in formation of **8** requires[21] that reaction 4 be important; otherwise only a secondary isotope effect should have been observed.

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(18) A similar situation appears to occur in the photolysis of benzophenone in benzene[19] where the major process is suggested to be efficient addition of triplet benzophenone to benzene. The resulting diradical reverses no less efficiently to benzophenone and benzene. An inefficient but not completely reversible process ($\phi \sim 0.005$) involving H abstraction from benzene competes and is responsible for the formation of benzpinacol, biphenyl, and bis(phenyl)diphenylcarbinol.

(19) (a) J. A. Bell and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 528 (1963); (b) J. Saltiel, H. C. Curtis, and B. Jones, *Mol. Photochem.*, **2**, 331 (1970); (c) J. Dedinas, *J. Phys. Chem.*, **75**, 181 (1971); (d) A. V. Buettner and J. Dedinas, *ibid.*, **75**, 187 (1971); (e) D. I. Schuster, T. M. Weil, and M. R. Topp, *Chem. Commun.*, 1212 (1971); *cf.* also D. I. Schuster and D. F. Brizzarola, *J. Amer. Chem. Soc.*, **92**, 4357 (1970).

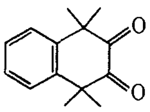
(20) Similar distributions were observed[19b,c] in the biphenyls formed by irradiation of benzophenone in benzene–deuteriobenzene mixtures. The isotope effect in formation of the phenyl radical was estimated to be between 4 and 12. It might be noted that addition of radical **10** to benzene and subsequent cleavage, oxidation, etc.,[18e] to biphenyl would also explain the observed results.

(21) It should be noted that spin conservation requires that the diradical **10** be formed initially as a triplet. The exothermic reaction 5 leading to product will not occur until after spin reorganization thus providing time during which reversal to starting material can occur. For a discussion of the time scale for such spin reorganization, see P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

It seems likely that the primary quantum yield for reaction 3, addition of PQ^3 to benzene, is close to unity as observed[18] in the reaction of triplet benzophenone with benzene. If this is correct and the hydrogen abstraction from benzene is not reversible, addition of PQ^3 to benzene is approximately 35 times faster than hydrogen abstraction.

The mechanism suggested above provides a reasonable explanation for all of the results obtained. However, it should be noted that an alternate proposal can also be considered. When a hydrogen atom is transferred from benzene to triplet PQ, a geminate radical pair is formed within a "solvent cage." This radical pair may retain triplet character as required by spin conservation. In addition to reversal to starting materials, the pair of radicals may couple after spin reorganization or diffuse apart to yield products upon subsequent encounters. All of the results can be explained if it be assumed that phenyl radicals in the solvent cage are not intercepted by iodine and that all adduct is formed from radical pairs which have not diffused apart.[22] The results obtained with chlorobenzene would then require that H abstraction occur exclusively from the para position of chlorobenzene. The resulting *p*-chlorophenyl radicals could add indiscriminately to *p*-chlorobenzene to give *three* dichlorobiphenyls. Such a mechanism does not require that the primary quantum yield for PQ^3 reaction with benzene be unity; the low (relative to other PQ reactions) quantum yield observed with benzene could reflect the greater strength of the C–H bond in benzene.

The photoreduction of 1,1,4,4-tetramethyl-2,3-tetralindione (**12**) observed[23] in benzene solution has been attributed to hydrogen atom abstraction by triplet **12** from ground state **12**. We have found that irradiations of **12** and of camphorquinone (**13**) in degassed benzene solutions produce complex product mixtures which contain biphenyl as well as products of reduction of the α diketones. Clearly, benzene cannot be classed as an inert solvent in many photochemical reactions and care should be exercised in interpretation of results when it is used.



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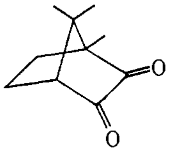

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Experimental Section

Materials. 9,10-Phenanthrenequinone (Aldrich) was washed through Florisil with ethyl acetate and recrystallized from ethyl acetate. Benzene (BDH Chemicals Analar grade) was distilled through a 70-cm tantalum wire spiral column and freshly boiled before use. Anthracene (Eastman White Label) was purified by chromatography on alumina followed by crystallization from methanol. Hexadeuteriobenzene (Fluka, 99.5%) was used as received.

Quantum Yield Determinations. Solutions about 3.3×10^{-4} *M* PQ in benzene in 1-cm square Pyrex cells were degassed by at least five freeze-pump-thaw cycles (final vacuum 1μ). Irradiations were performed with a 125-W medium-pressure mercury vapor lamp using Corning color filters to isolate the 366- and 436-nm lines and Jena interference filters for the 313- and 404-nm lines. Ferrioxalate actinometry[24] was used. Total light intensity incident on the 9 × 25 mm unmasked area of each cell was $1\text{-}4 \times 10^{-7}$ einstein/min.

Irradiation of PQ in Benzene Solution. A suspension of 1 g of PQ in 200 ml of freshly boiled benzene under nitrogen was irradiated with light from a water-cooled 450-W immersion lamp (Hanovia L679A) filtered through a filter sleeve which eliminated radiation below 370 nm. After 5 days, during which a slow stream of nitrogen was bubbled through the solution, irradiation was terminated and the clear, wine-red solution was concentrated *in vacuo* without heat. The residue was taken up in 1:1 benzene–hexane and filtered to afford 460 mg (21%) of black phenanthrenequinhydrone.

The filtrate was chromatographed on 70 g of Florisil. Elution with hexane gave 135 mg (18%) of biphenyl, mp 67–68°. Elution with 30% benzene–hexane gave 257 mg (19%) of **8**: mp 133–135°. The analytical sample of the monophenyl ether of 9,10-dihydroxyphenanthrene was obtained by crystallization from methylene chloride–hexane: mp 140–141° (lit.[11a] mp 140–141°); uv (dioxane) 256 (50,000), 274 (sh, 16,500), 297 (9900), 307 (9900), 327 (sh, 910), 345 (1600), 362 nm (1450); ir (KBr) 2.95, 6.15, 6.28 μ; nmr ($CDCl_3$) complex multiplets at δ 7–7.8 and 8.2–8.8 ppm.

Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93; mol wt, 286. Found: C, 83.54; H, 5.06; M^+, 286.

Elution with pure benzene gave 107 mg of amorphous material which could not be obtained crystalline. Elution with ethyl acetate gave 300 mg (30%) of PQ.

Irradiations of PQ in Benzene–Benzene-d_6 Mixtures. Solutions of about 20 mg of PQ in 2–3 ml of a mixture containing weighed amounts of benzene and benzene-d_6 were degassed and sealed off. Solutions were then irradiated for 72–96 hr with light from a 200-W high-pressure lamp (Osram HBO 200 W) filtered by a Corning cutoff filter to remove light below 390 nm. For determination of isotopic composition of biphenyls, the solution was concentrated to a small volume and the biphenyl fraction isolated by gas chromatography and analyzed by mass spectrometry (Table I). For isotopic composition of adducts, a sample of crude product was treated with a few drops of methanol, evaporated to dryness, and analyzed by mass spectrometry. In one case, the total crude product was chromatographed as described above and the purified adduct analyzed with identical results. For a 1.13:1 molar ratio of benzene-d_6: benzene the ratio of 291:286 peaks was 1:1.85. Using a 2:1 ratio of benzene-d_6: benzene the ratio was 1:1.

Irradiation of PQ in Benzene in the Presence of Iodine. A solution containing PQ (2.0 mg) and iodine (2.4 mg) in 3 ml of benzene in a 1-cm square Pyrex cell was degassed and irradiated using an Osram 200-W point source and a 404-nm Jena interference filter for 72 hr. Gas chromatographic analysis on two different columns showed a peak with the same retention time as iodobenzene (15% Carbowax 20M, 90°, 30 ml of N_2/min, retention time 8 min and 5% SE-30, 65°, 5 ml of N_2/min, retention time 7.5 min) and no peak corresponding to biphenyl. The yield of iodobenzene was 19% based on comparison of peak areas with those obtained from solutions of known concentration.

The remaining solution was concentrated to a small volume and a tlc chromatogram (silica gel, 1:1 chloroform–benzene) gave a streak (R_f 0.7) corresponding to **8**. This was scraped from the plate and eluted with 3 ml of ethanol and the uv spectrum determined it to be the adduct. The yield, based on absorbance, was 20%.

Irradiation of PQ in Chlorobenzene. A suspension of PQ (500 mg) in freshly distilled chlorobenzene (155 ml) was irradiated as described above for the reaction with benzene. Irradiation was stopped after 11 days when the uv spectrum of an aliquot indicated that reaction had become very slow. The excess chlorobenzene was evaporated at 70° (30 mm) and the residue chromatographed on 35 g of Florisil. Elution with hexane afforded 180 mg (34%) of mixed dichlorobiphenyls which showed three overlapping peaks (all of *m/e* 198) upon gas chromatographic analysis (1% XE-60, 160°, 30 ml of N_2/min).

Elution with 10% benzene in hexane afforded 107 mg (14%) of crystalline adduct **9**. The analytical sample of the mono-*p*-chlorophenyl ether of 9,10-dihydroxyphenanthrene was obtained by crystallization from methylene chloride–hexane: mp 139–139.5°; uv

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[22] The photoaddition of camphorquinone and *p*-xylene appears, in fact, to involve only such geminate radical pairs. When the semidione and *p*-methylbenzyl radicals which are intermediates are not generated in proximity, radical disproportionation and dimerization proceed to the exclusion of coupling between unlike radicals. M. B. Rubin, *Tetrahedron Lett.*, 3931 (1969); *cf.* also S. A. Weiner, *J. Amer. Chem. Soc.*, **93**, 425 (1971).

[23] G. E. Gream, J. C. Paice, and C. C. R. Ramsay, *Aust. J. Chem.*, 20, 1671 (1967).

[24] C. J. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(dioxane) 256 (60,000), 274 (sh), 296 (12,750), 306 (12,750), 326 (sh, 1150), 342 (1840), 364 nm (2000); ir (KBr) 3.1, 6.15, 6.23, 6.3 μ; nmr ($CDCl_3$) δ 5.95 (1 H, disappeared upon addition of D_2O), 6.90 (d, $J = 9$ Hz, 1 H), 7.17 (d, $J = 9$, 1 H), 7.35–7.85 (m, 6 H), 8.2–8.8 (m, 2 H).

Anal. Calcd for $C_{20}H_{13}O_2Cl$: C, 74.89; H, 4.08; mol wt, 320. Found: C, 75.16; H, 4.05; M^+, 320.

Elution with benzene gave 60 mg of amorphous material which was not characterized. Elution with ethyl acetate gave 200 mg of PQ (40%).

Spiropentylcarbinyl Cation Rearrangement. Stereochemistry of Nucleophilic Attack in a Cyclopropylcarbinyl to Cyclobutyl Cation Rearrangement and Stereochemistry of the Ring Opening of the 1-Cyclopropylcyclopropyl Cation[1]

Joseph J. Gajewski*[2] **and John P. Oberdier**

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401.

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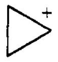
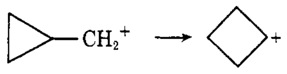
Abstract: Buffered acetolysis of spiropentylcarbinyl tosylate at room temperature gave 5-spirohexyl acetate (**11**), 1-cyclopropylcyclopropyl acetate (**12**), and 2-cyclopropylallyl acetate (**13**) as major identifiable products. Deuterium labeling of the carbinyl carbon verified the hypothesis that **11** was the result of a cyclopropylcarbinyl to cyclobutyl cation rearrangement with C_3 as the migrating carbon while **12** and **13** were the result of a cyclopropylcarbinyl to cyclopropylcarbinyl cation rearrangement with the latter material resulting from subsequent opening of the derived 1-cyclopropylcyclopropyl cation. Acetolysis of 4-methylspiropentylcarbinyl tosylates revealed that the cyclopropylcarbinyl to cyclobutyl rearrangement proceeded with predominant inversion at the migration origin upon nucleophilic attack and that the opening of the 1-cyclopropylcyclopropyl cation was highly stereospecific but did not depend on the orientation of the carbon leaving group, thus leading to the conclusion that the cyclopropyl cation was, in fact, planar. The magnitude and origin of the stabilization of the cyclopropyl cation by an adjacent cyclopropane ring is discussed.

Foremost among small ring cationic ion systems are cyclopropyl[3] and cyclopropylcarbinyl ones[4] (**1** and **2**) because of their surprising and unique reactivity among saturated systems and the relationship of their reactivity and reaction pathways to early[5] and recent theory.[6]

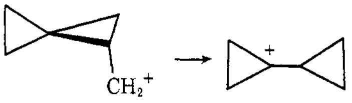


1



2 **3**

When this work was begun, little was known of the stereochemistry of nucleophilic attack at the migration origin in the cyclopropylcarbinyl to cyclobutyl cation (**3**) rearrangement. This was the case because Roberts very early[4] and Schleyer later on[7] had shown that methyl stereochemical labels placed on the system to answer this question so severely perturbed it that the product emerged with the stereochemical label on the carbinyl carbon. Since a nonclassical or delocalized cation had been invoked for this reaction,[3] and since the delocalized ion hypothesis predicts inversion,[5] the test appeared to be crucial. We attempted to resolve the problem by using the spiropentylcarbinyl system **4** where it was hoped that the additional cyclopropyl group would not lend itself to stabilization of the cation on the carbinyl carbon in **5**. Our concern, however, was deeper than simply testing the nonclassical ion hypothesis. We had already shown[8] that in a similar rearranging system, namely the cyclobutylcarbinyl to cyclopentyl cation, where nonclassical intermediates appeared likely on the basis of fast solvolytic rates, that *net retention* (67%) at the migration origin was observed; thus, the Ingold rule[5] was violated for some reason, and so our concern spread to the lower homolog. As our work proceeded others, Dauben[9] particularly, and Schleyer[4b] later, but most elegantly, showed that complete inversion at the migration origin occurred in the formation of the cyclobutyl product from the cyclopropylcarbinyl system.



4 **5**

Our results reported below confirm this but also lead to a study of the opening of cyclopropyl cations when stabilized by adjacent cyclopropane rings since

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[1] Taken from the Thesis of J. P. O., submitted in partial fulfillment of the M.S. degree requirements of Indiana University, Sept 1971.

[2] Fellow of the Alfred P. Sloan Foundation, 1971–1973.

[3] For review see C. H. De Puy, *Accounts Chem. Res.*, 1, 33 (1968).

[4] For reviews see (a) R. Breslow in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963. (b) References in F. Majerski and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 665 (1971).

[5] See C. K. Ingold in "Structure and Mechanisms in Organic Chemistry," 1st ed, Cornell University Press, Ithaca, N. Y., 1953, Chapter 14.

[6] For a summary of 5 years of development see R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[7] P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

[8] J. J. Gajewski, R. E. Lyle, and R. P. Gajewski, *Tetrahedron Lett.*, 1189 (1970).

[9] W. G. Dauben and E. I. Aoyagi, *Tetrahedron*, **26**, 1249 (1970).