fer from the foregoing results that the tetraalkoxyphosphoranyl radicals also have a distorted trigonal-bipyramidal structure. The latter is consistent with the elegant chemical experiments which recently showed the retention of stereochemistry and nonequivalency of the alkoxy groups in these radicals.[23]

Finally, these esr results only reveal the steady-state concentration of various radicals extant in solution. Nonetheless, by utilizing different substrates and varying conditions, the importance of various homolytic processes can be inferred by the appearance and absence of certain paramagnetic species. As a result, a consistent picture is derived for homolytic substitution on phosphorus involving an addition–elimination mechanism.[24] Competitive esr spectroscopy and time intermittency can be used to make such studies quantitative, and recent studies[25] have shown that fragmentation (eq 17) of a phosphoranyl intermediate can proceed with a rate constant of at least 1.3×10^6 sec^{-1} at 30°.

$$(EtO)_3\dot{P}OBu^t \longrightarrow (EtO)_3PO + Bu^t\cdot \qquad (17)$$

Acknowledgments. We wish to thank Dr. G. Parshall, Dr. E. L. Muetterties, and Dr. J. Stille for valuable discussions. Dr. G. Parshall kindly provided us with a sample of dimethylphenoxyphosphine. We are also grateful to Mr. M. Cushing for excellent technical assistance. P. J. K. would like to thank Professor D. Hadži (Ljubljana) for the hospitality extended him during the later stages of this work under a program of exchange sponsored by the National Academy of Sciences and the Council of Yugoslav Academies. J. K. K. also thanks the National Science Foundation for financial support.

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(23) W. G. Bentrude and R. A. Wielesek, *J. Amer. Chem. Soc.*, **91**, 2406 (1969); W. G. Bentrude, P. E. Rusek, Jr., and J. H. Hargis, *Chem. Commun.*, 296 (1969); W. G. Bentrude and T. B. Min, private communication.

(24) These experiments, of course, do not rule out the participation of direct displacement processes.

(25) A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem., Int. Ed. Engl.*, **10**, 738 (1971). Additional kinetic esr studies on phosphoranyl radicals are in progress (A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin* 2, in press; G. B. Watts, D. Griller, and K. U. Ingold, *J. Amer. Chem. Soc.*, in press). Professor Davies and collaborators have recently prepared Et_2POEt and thence $Et_2\dot{P}(OEt)OBu^t$, which shows $a(P) = 707$ G, supporting our identification of the second generation radicals as dialkoxyphosphoranyls.

Photochemistry of Stilbenes. VI.[1] Steric Effects on the Photocyclizations of Some Meta-Substituted Stilbenes[2]

Frank B. Mallory* and Clelia W. Mallory

Contribution from the Department of Chemistry,
Bryn Mawr College, Bryn Mawr, Pennsylvania 19010.

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Abstract: The isomer ratios of the 2- and 4-substituted phenanthrenes produced by the photocyclization in the presence of iodine of a series of meta-substituted stilbenes were determined to assess the importance of steric effects on these photoreactions. The irradiations of *m*-methyl-, *m*-chloro-, and *m*-trifluoromethylstilbene each gave product ratios near unity. From these results and other arguments it is concluded that the more crowded 4-substituted product and the less crowded 2-substituted product are formed at almost identical rates in each case, implying an early transition state for cyclization. The photocyclization of *m,m'*-dimethylstilbene revealed a modest steric hindrance to the formation of one of the three products, 4,5-dimethylphenanthrene; analogous behavior was found for the sterically related 2-(*m*-methylstyryl)naphthalene. In addition, the relative amount of 4,5-dimethylphenanthrene produced from *m,m'*-dimethylstilbene varied from 0 to 18% depending on the iodine concentration, indicating that thermal ring opening of the dihydrophenanthrene precursor is competitive with its oxidative trapping.

The formation of phenanthrenes and related polynuclear aromatic molecules by the ultraviolet irradiation of stilbenes or stilbene derivatives in solutions containing an oxidant like iodine or oxygen has been extensively studied, and many aspects of the scope, mechanism, and preparative utility of this photocyclization are known.[3] Only a brief summary of portions of this knowledge[4] will be given here, using the parent system as an example (see Scheme I). Thus, ultraviolet irradiation of solutions[5] of either *trans*-stilbene (**1**) or *cis*-stilbene (**2**) in the absence of an oxidant leads to the establishment of a photostationary mixture containing the two stilbenes together with the isomeric 4a,4b-

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(1) For Part V, see F. B. Mallory and C. S. Wood, *Tetrahedron Lett.*, 2643 (1965).

(2) Presented in part at the First Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 3, 1966, and also at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., Apr 1–5, 1968, Abstract P-217.

(3) For reviews, see (a) F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 247–282; (b) M. Scholz, F. Dietz, and M. Mühlstädt, *Z. Chem.*, **7**, 329 (1967); (c) W. H. Laarhoven, Th. J. H. M. Cuppen, and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **87**, 687 (1968); and (d) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

(4) (a) H. Stegemeyer, *Z. Naturforsch., B*, **17**, 153 (1962); (b) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Amer. Chem. Soc.*, **84**, 4361 (1962); (c) W. M. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 829 (1963); (d) F. B. Mallory, C. S. Wood, and J. T. Gordon, *ibid.*, **86**, 3094 (1964); (e) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964); (f) A. A. Lamola, G. S. Hammond, and F. B. Mallory, *Photochem. Photobiol.*, **4**, 259 (1965); (g) K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967); (h) J. Saltiel, *J. Amer. Chem. Soc.*, **90**, 6394 (1968); (i) A. Bylina and Z. R. Grabowski, *Trans. Faraday Soc.*, **65**, 458 (1969).

(5) Concentrations less than about 0.05 *M* are generally used to avoid the formation of tetraphenylcyclobutanes by photodimerization.

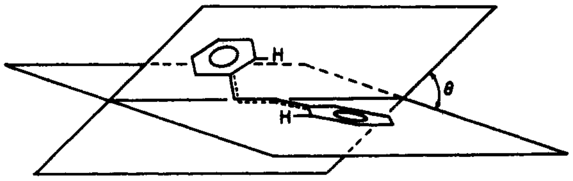
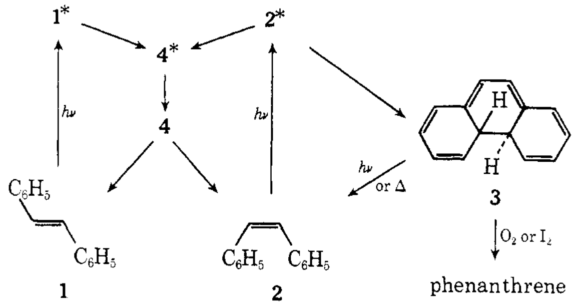


Figure 1. An approximate representation of *cis*-stilbene in its lowest excited singlet state (2*).

Scheme I



dihydrophenanthrene (**3**).[6] This high-energy isomer, which is formed exclusively from *cis*-stilbene[7] in its excited singlet state (**2***) with a quantum yield of about 0.1, undergoes both thermal and photochemical ring opening to regenerate **2** and also can be trapped efficiently in the presence of oxygen or iodine to give phenanthrene (together with hydrogen peroxide or hydrogen iodide) with a chemical yield of more than 90%. Besides cyclization, the other principal fate of **2*** under the conditions of interest[8] is to undergo radiationless decay proceeding by way of a twisted species (**4***) that subsequently gives either **1** or **2**. In terms of the approximate representation of **2*** given in Figure 1, cyclization involves a decrease in θ (among other structural changes), while the competing radiationless decay involves an increase in θ (to a value of about 90°). In comparison to **2**, **2*** is thought to have a greater π-electron density at the ortho carbons (which accounts for photocyclization), a smaller π-bond order between the olefinic carbons (which accounts for cis–trans photoisomerization), and a greater π-bond order for the C-1–C-α and C-1′–C-α' bonds.

Results and Discussion

In order to gain more insight into the mechanistic details and the structure–reactivity relationships for ring closures of the **2*** → **3** type, we undertook a study of the photocyclizations of some meta-substituted stilbenes. The relevant reaction pathways[9] for the case of *cis-m*-methylstilbene (**5**) are indicated in Scheme II. The two ground-state conformers, **5a** and **5b**, are considered to be in rapid equilibrium; there is very little π bonding between C-1 and C-α and consequently the barrier for the **5a** $\rightleftarrows$ **5b** interconversion is small. On the other hand, the interconversion between the corresponding excited singlet-state molecules, **5a*** and **5b***, is not expected to be kinetically competitive with the radiationless decay and the cyclization processes of **5a*** and **5b***; because of the increased π bonding between C-1 and C-α it is believed that more thermal activation energy would be required to surmount the barrier for the **5a*** $\rightleftarrows$ **5b*** interconversion than can be acquired by these molecules during the extremely short excited singlet lifetimes that are characteristic of *cis*-stilbenes.

Table I. Compositions of the Product Mixtures from the Photocyclizations of Some Meta-Substituted Stilbenes[a]

Stilbene	Substituents	Product isomer distribution[b]		
5	*m*-CH_3	**7a**, 51%	**7b**, 49%	
8	*m*-Cl	**10a**, 52%[c]	**10b**, 48%[c]	
9	*m*-CF_3	**11a**, 52%[c]	**11b**, 48%[c]	
12	*m*-CH_3, *m*′-CH_3	**14a**, 28%[d]	**14b**, 54%[d]	**14c**, 18%[d]
12	*m*-CH_3, *m*′-CH_3	**14a**, 33%[e]	**14b**, 63%[e]	**14c**, 4%[e]
17	*m*-CH_3, *m*′-benzo	**19a**, 61%	**19b**, 39%	

[a] Air-saturated cyclohexane solutions (3 ml) of the stilbene (0.01 *M*, initially the trans isomer) and iodine (ranging from 5×10^{-4} to 5×10^{-2} *M*) were irradiated in Pyrex tubes on a rotating turntable with a 400-W General Electric mercury lamp housed in a water-cooled Pyrex probe mounted at the center of the turntable. Product mixtures were analyzed quantitatively (Disc integrator) by gas–liquid chromatography with a 1.8 m × 6 mm glass column packed with 2% neopentyl glycol succinate on 80–100 mesh Gas Chrom S at fixed temperatures in the 155–230° range. [b] The tabulated product percentages are averages from at least three different irradiations; the values are considered reliable within about ±0.5. [c] The **10a**/**10b** and **11a**/**11b** ratios increased during the irradiations, typically from about 52/48 at 5–10% conversion to about 55/45 at 80–90% conversion; independent experiments indicated that the **10b** and **11b** isomers were slowly destroyed under the irradiation conditions. [d] With 5×10^{-2} *M* iodine. [e] With 5×10^{-4} *M* iodine.

The final products in this case, the phenanthrenes **7a** and **7b**, were obtained in a ratio of 51/49 (see Table I). This result is intriguing since it suggests that the greater steric crowding in **7b** as compared to **7a** does not play a major role in determining the partitioning between the two reaction pathways. However, before this overall product ratio can be confidently related to the quantity of mechanistic interest, the relative rate of the **5a*** → **6a** cyclization as compared to that of the **5b*** → **6b** cyclization, four other factors must be evaluated: the stabilities of **7a** and **7b** under the reaction conditions; the efficiencies of the two oxidative trapping reactions, **6a** → **7a** and **6b** → **7b**; the relative numbers of **5a*** and **5b*** molecules produced by irradiation of the mixture of **5a** and **5b**; and the relative rates of radiationless decay of **5a*** and **5b***.

To provide evidence concerning the first two factors, we irradiated a series of solutions of **5** under the conditions specified in Table I with iodine concentrations ranging from 5×10^{-4} to 5×10^{-2} *M* and found the same **7a**/**7b** ratio, 51/49, throughout this range. We interpret this to indicate that the dihydrophenanthrenes

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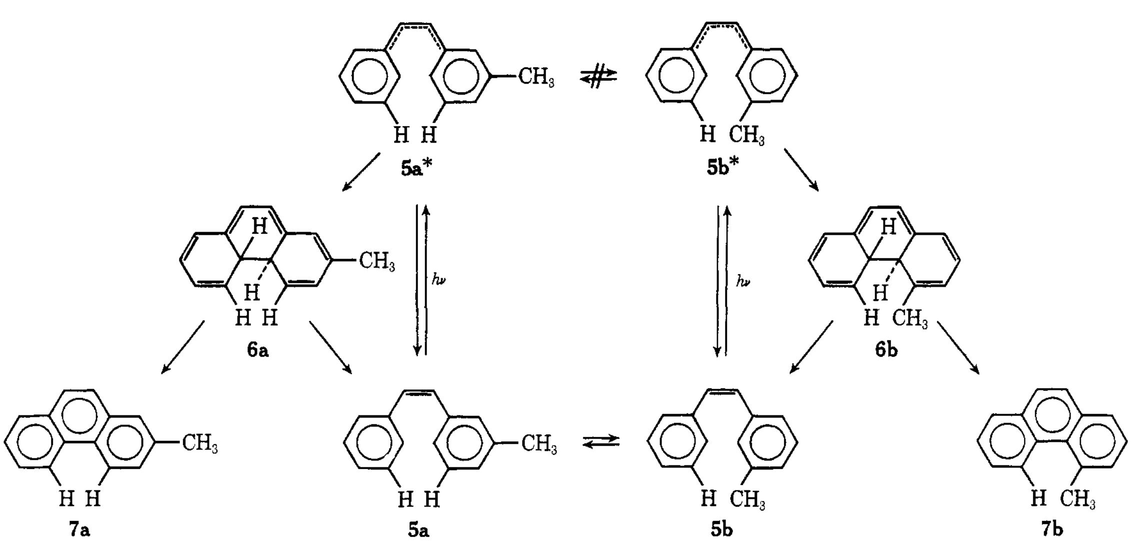
[6] The trans configuration is indicated for 3 in Scheme I (and Figure 4) on the basis of theoretical expectations: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., 1970, p 52. See also A. Bromberg and K. Muszkat, *J. Amer. Chem. Soc.*, **91**, 2860 (1969); T. D. Doyle, N. Filipescu, W. R. Benson, and D. Banes, *ibid.*, **92**, 6371 (1970).

[7] The photocyclization of a stilbene is normally carried out starting with the synthetically more accessible trans isomer; the overall photoconversion to the corresponding phenanthrene involves photoisomerization to the cis isomer as the first step.

[8] Fluorescence of 2* becomes significant only at very low temperatures.

[9] In Scheme II (and also in Schemes III and V) the radiationless decay paths for the excited singlet-state molecules are indicated for simplicity by single arrows, but it should be understood that the process in each case involves twisting around the central bond to a perpendicular configuration followed by partitioning between the cis and trans ground-state isomers.

Scheme II



6a and **6b** were both oxidatively trapped with unit efficiency in all of these experiments. Furthermore, the **7a**/**7b** ratio remained constant during the course of each irradiation, which suggests that these two phenanthrenes do not differ significantly in their stabilities under the reaction conditions.[10]

Regarding the third factor, it will be seen from the following argument that as a reasonable approximation one can consider that the equilibrium constant for the **5a** ⇄ **5b** interconversion is unity and the ultraviolet absorption spectra of **5a** and **5b** are identical, so that **5a*** and **5b*** are produced at equal rates. In the absence of detailed structural data for the *cis*-stilbene system, we have used an approximate theoretical model to evaluate the question of possible steric influences on the energy of **5a** relative to **5b**. The parameters assumed for this model are given in Table II, and the results of some calculations using these parameters are given in Table III. The calculated distance between the two interior meta hydrogens in **5a** is 4.1 Å, which also turns out to be the distance between the interior meta hydrogen and the methyl group in **5b**. In each case the estimated distance exceeds the sum of the van der Waals radii for the two groups (3.0 Å for two hydrogens and 3.8 Å for hydrogen and methyl), so no destabilizing steric interaction between meta groups is expected. Therefore, **5a** and **5b** should be virtually equal in energy (hence equal in Boltzmann population) and should have virtually the same angle of conrotatory twist about the C-1-C-α and C-1′-C-α′ bonds (hence equal absorption spectra).[11]

Table II. Assumed Structural Parameters for Some *cis*-Stilbenes

Bond distances, Å	Aromatic C–C, 1.40; C=C, 1.34; =C–C, 1.48; aromatic C–H, 1.08; C–CH$_3$, 1.51; C–CF$_3$, 1.51;[a] C–Cl, 1.70
Bond angles	Aromatic ring, 120°; C=C–C, 128°;[b] aromatic–olefinic dihedral angle, 30°[c]
van der Waals radii, Å	H, 1.5;[d] Cl, 1.8; CH$_3$, 2.3;[e] CF$_3$, 2.3[e]

[a] Chosen equal to the C–CH$_3$ distance by analogy with results for other compounds as cited by C. H. Chang, A. L. Andreassen, and S. H. Bauer, *J. Org. Chem.*, **36**, 920 (1971). [b] Estimated by analogy with *trans*-stilbene: J. M. Robertson and I. Woodward, *Proc. Roy. Soc., Ser. A*, **162**, 568 (1937). [c] D. L. Beveridge and H. H. Jaffé, *J. Amer. Chem. Soc.*, **87**, 5340 (1965). [d] See N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *ibid.*, **93**, 1637 (1971), and references cited therein. [e] Estimated from bond distances (C–H, 1.10 Å; C–F, 1.33 Å) and van der Waals radii (H, 1.5 Å; F, 1.35 Å), assuming tetrahedral angles.

Table III. Sums of van der Waals Radii and Calculated Distances of Separation for Meta Substituents in Some Model *cis*-Stilbenes[a]

Structure	Interior meta substituents	Calculated distance, Å	Sum of van der Waals radii, Å
5a, 8a, 9a, 12a	H, H	4.1$_0$	3.0
5b, 12b	H, CH$_3$	4.1$_1$	3.8
8b	H, Cl	4.1$_3$	3.3
9b	H, CF$_3$	4.1$_1$	3.8
12c	CH$_3$, CH$_3$	4.1$_0$	4.6

[a] The tabulated values are based on the parameters given in Table II.

Finally, with regard to the fourth factor, we consider it likely that the excited-state molecules **5a*** and **5b*** are also, like **5a** and **5b**, essentially free[11] from van der Waals interactions between interior meta groups.[13] Since the twisting motion involved in the radiationless decay process leads to an even greater separation between these groups, we see no reason to expect a significant difference in the rates at which **5a*** and **5b*** undergo this process.

In view of the preceding analysis, it can indeed be concluded from the fact that almost equal amounts of **7a** and **7b** are produced by the irradiation of **5** that the

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(10) When the irradiations were carried out without a Pyrex filter and in the absence of iodine (*i.e.*, with dissolved oxygen as the only oxidant), the **7a**/**7b** ratio was found to increase from 53/47 at 6% conversion to 55/45 at 86% conversion as a result of selective destruction of **7b**; analogous behavior was observed for the other stilbene systems studied.

(11) Actually, the meta–meta′ van der Waals interactions would be slightly stabilizing, with the methyl–hydrogen interaction in **5b** calculated[12] to be 0.02 kcal/mol more attractive than the hydrogen–hydrogen interaction in **5a**; this would translate into a Boltzmann population of about 49% **5a** and 51% **5b**.

(12) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(13) Although the aromatic–olefinic dihedral angles in **5a*** and **5b*** may be considerably less than the 30° angles assumed for **5a** and **5b**, which would tend to shorten the interior meta–meta′ distance, this should be compensated for by a twist around the central carbon–carbon bond in **5a*** and **5b*** (as implied in Figure 1).

$5a^* \rightarrow 6a$ and $5b^* \rightarrow 6b$ transformations proceed with very similar rates.

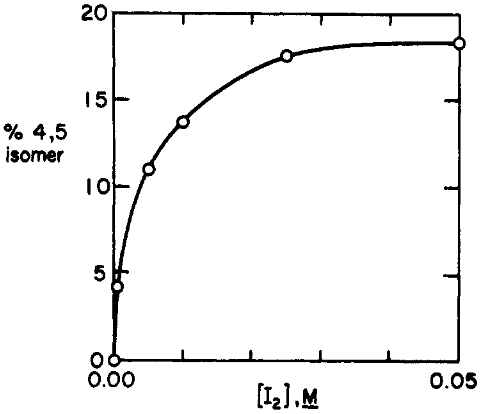
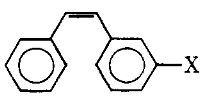


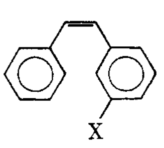
Figure 2. The percentage of 4,5-dimethylphenanthrene (**14c**) in the product mixture obtained by ultraviolet irradiation at 25° of 0.01 *M* solutions of *trans-m,m'*-dimethylstilbene as a function of the concentration of iodine in these solutions.

In contrast to the excited *cis*-stilbenes **5a*** and **5b***, the dihydrophenanthrenes **6a** and **6b** are clearly destabilized as a result of repulsive interactions between the groups attached to C-4 and C-5, and this destabilization is more pronounced in **6b** than in **6a**. Thus, the distance between the C-4 and C-5 hydrogens in **6a** is judged from a Dreiding model to be about 2.0 Å, which is 1.0 Å less than the sum of the van der Waals radii, while the distance between the C-4 methyl carbon and the C-5 hydrogen in **6b** is similarly judged to be about 1.8 Å, which is 2.0 Å less than the van der Waals sum. Although the molecules would distort from the Drieding model structures to diminish these violations of van der Waals radii, the prediction of greater destabilization of **6b** compared to **6a** is surely reliable. So during the $5b^* \rightarrow 6b$ transformation a greater amount of steric crowding develops than during the $5a^* \rightarrow 6a$ transformation. Since these two reactions appear to proceed with nearly the same rate, we infer that the transition state[14] for the $5b^* \rightarrow 6b$ ring closure, and, by analogy, for all ring closures of the $2^* \rightarrow 3$ type, occurs early along the reaction coordinate when the structure is still closely related to that of the uncrowded excited-state reactant.

This inference is supported by our investigations of two other meta-substituted stilbenes, *cis-m*-chlorostilbene (**8a** and **8b**) and *cis-m*-trifluoromethylstilbene (**9a** and **9b**), for which the product ratios of the corresponding phenanthrenes, 2- and 4-chlorophenanthrene (**10a** and **10b**, respectively) and 2- and 4-trifluoromethylphenanthrene (**11a** and **11b**, respectively), are also very near unity (see Table I). The reaction pathways for these two stilbenes are exactly analogous to those shown in Scheme II for the methyl compound, the calculated distances between interior meta groups in **8a**, **8b**, **9a**, and **9b** are all greater than the sums of the van der Waals radii for the two groups (see Table III), and all of the arguments presented above for the methyl system also apply to the chloro and trifluoromethyl systems. Thus, we conclude from the **10a**/**10b** and **11a**/**11b** product ratios, 52/48 in each case, that the rates of cyclization of **8b*** and **9b*** are essentially the same as those of **8a*** and **9a***, respectively. Once again, the lack of steric retardation is in accord with an early transition state for cyclization.



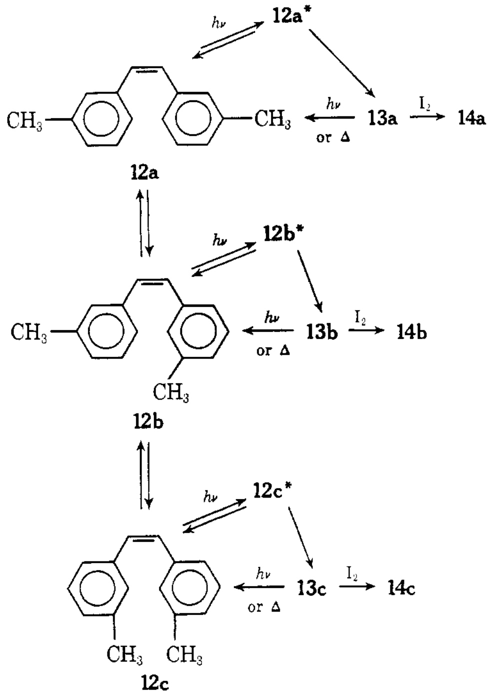
8a, X = Cl
9a, X = CF_3



8b, X = Cl
9b, X = CF_3

We next turned our attention to the *cis-m,m'*-dimethylstilbene system (**12**) in order to explore the consequences of the more severe steric requirements associated with the formation of 4,5-dimethylphenanthrene. There are three equilibrating ground-state conformers to be considered in this system, **12a**, **12b**, and **12c**. These three conformers undergo photocyclization to the corresponding three dihydrophenanthrenes, **13a**, **13b**, and **13c**, which are oxidatively converted, in turn, to 2,7-dimethylphenanthrene (**14a**), 2,5-dimethylphenanthrene (**14b**), and 4,5-dimethylphenanthrene (**14c**) as shown in Scheme III.[10]

Scheme III



Considering first only the photocyclization of the **12a** and **12b** conformers in the dimethyl system, one would expect a quantitative correspondence with the photocyclization of the **5a** and **5b** conformers in the monomethyl system, except for a statistical factor of 2 in favor of the photocyclization of **12b** (there are two equivalent ways to have one methyl group "inside" and the other "outside," so as a first approximation there will be twice as much **12b** as **12a** in the equilibrium mixture of conformers). In exact accord with this expectation, the **14a**/**14b** product ratio was found (Table I) to be 0.52, independent of iodine concentration, as compared with the **7a**/**7b** product ratio of 51/49 = 1.04.

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(14) The existence of a thermal energy barrier for cyclization was demonstrated by the finding that at low temperature (77°K) the photocyclization of *cis*-stilbene ($2^* \rightarrow 3$) is inhibited and instead fluorescence ($2^* \rightarrow 2 + h\nu$) is observed.[4f] In a detailed quantitative study of the related 1,2-diphenylcyclopentene system the analogous barrier was evaluated as 3.1 kcal/mol.[4g]

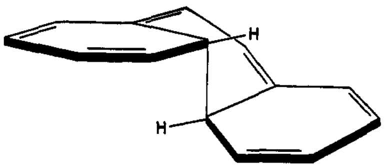

Figure 3. An approximate representation of the skewed dihydrophenanthrene geometry that is thought to characterize both the transition state (**15**) for the adiabatic ground-state conversion of dihydrophenanthrene (**3**) to *cis*-stilbene (**2**) and also the excited-state intermediate (**15***) whose role is discussed in the text.

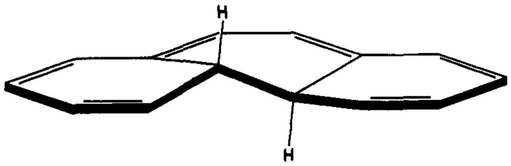

Figure 4. An approximate representation of the normal geometry of ground-state dihydrophenanthrene (**3**).

The photocyclization of the **12c** conformer appeared to differ in two respects from the other photocyclizations that we have considered so far. First, the relative yield of the corresponding phenanthrene, **14c**, was strongly dependent on the concentration of iodine employed (see Figure 2), which we attribute to a competition between the bimolecular trapping and the unimolecular thermal ring opening of the dihydrophenanthrene, **13c**. The strain energy associated with the serious crowding of the two methyl groups in **13c** should be roughly equal in magnitude to that of 4,5-dimethylphenanthrene (**14c**), for which a value of 12.1 kcal/mol has been established.[15] The thermal ring opening of **13c** should be markedly accelerated because this strain is relieved in the process. Consistent with this explanation, the relative amount of **14c** produced by the irradiation of **12** at an iodine concentration of 2.5×10^{-3} *M* varied with temperature from 10.8% at about 10° to 6.4% at about 35°. Since the curve in Figure 2 appears to reach a plateau at an iodine concentration of about 5×10^{-2} *M*, we feel that at this concentration essentially all of the **13c** that is formed is trapped to give **14c**.

The second interesting difference in the photocyclization of **12c** is that the yield of **13c** (as measured by the amount of **14c** obtained in the presence of 5×10^{-2} *M* iodine) is only 18%, which we consider to be significantly less than the 25% yield that would have been expected as a first approximation on purely statistical grounds. We have demonstrated that **14c** is not selectively destroyed under the irradiation conditions, and therefore we interpret its low yield as evidence for a steric effect of the methyl groups on the cyclization of **12c***. The magnitude of this effect can be evaluated by comparing the yields of **14a** and **14c** (see Table I); thus, the hindering effect of two inside methyl groups is worth a factor of 28/18 = 1.55, which contrasts with the factor of only 1.04 that was shown above to represent the effect of a single inside methyl group.

Crowding of the two methyl groups could contribute toward the observed steric effect on the formation of **14c** in several ways. On the basis of the geometrical model described in Tables II and III, the calculated distance between the methyl carbons in **12c** is 0.5 Å *less* than twice the van der Waals radius of the methyl group. The resulting destabilizing nonbonded interaction should make the equilibrium population of **12c** slightly less[12] than the statistical value of 25%; it should also increase the optimum aromatic–olefinic dihedral angle in **12c** compared with that in **12a** and **12b**, with the consequence that the ultraviolet extinction coefficients for **12c** would be slightly smaller than those for **12a** or **12b**. Thus, **12c** should be at a slight disadvantage relative to **12a** and **12b** in capturing photons. Another part of the overall effect can be accounted for by noting that the radiationless decay of **12c***, in which the twisting motion would relieve the destabilizing van der Waals repulsion between the two methyl groups, should occur at a slightly enhanced rate compared with that of either **12a*** or **12b***. A steric effect should also be operative on the cyclization step itself, the conversion of **12c*** to **13c**. Since our calculations indicate that the methyl–methyl interaction in **12c**, and presumably also in **12c***, is already governed by the steep repulsive part of the van der Waals interaction curve, any decrease in the methyl–methyl distance, which necessarily accompanies the **12c*** → **13c** transformation, is expected to lead to sharply increasing destabilization. Thus, the energy barrier for this cyclization would be raised, and as a consequence the fraction of the **12c*** molecules that would cyclize (in competition with radiationless decay) would be less.

In order to discuss one final way in which we feel that a steric effect can hinder the formation of a dihydrophenanthrene such as **13c**, we must digress briefly to introduce a more detailed picture of the cyclization of an excited *cis*-stilbene than has been considered so far. As will be discussed in depth in a subsequent publication in the present series, we believe that a transformation such as **2*** → **3** proceeds by way of an electronically excited intermediate, **15***,[16] that has a skewed dihydrophenanthrene geometry resembling that illustrated in Figure 3 (as compared to the normal dihydrophenanthrene geometry[17] indicated in Figure 4). This skewed geometry is thought to be very similar to that of the transition state, **15**, for the adiabatic ground-state isomerization of **3** to **2**, and the energy difference between **15*** and **15** is thought to be small. Therefore, the radiationless transition **15*** → **15**, which is believed to be the only fate of **15***, should be facile and should lead ultimately to nearly equal amounts of **2** and **3**. In our view, then, the part of Scheme I that deals with cyclization should be augmented as shown in Scheme IV.[18]

Returning now to the *m,m'*-dimethylstilbene system, we can consider the steric consequences of the intermediacy of the skewed dihydrophenanthrenes **16a***, **16b***, and **16c*** formed from **12a***, **12b***, and **12c***, respectively. As a result of methyl–methyl crowding in **16c***, the fraction of these excited molecules that would be diverted back to **12c** (with relief of this crowding) is expected to be slightly greater than the fractions of **16a***

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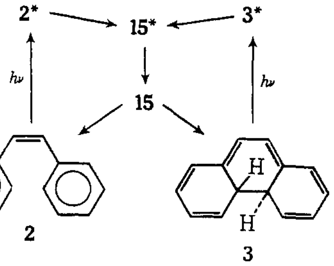
[15] H. A. Karnes, B. D. Kybett, M. H. Wilson, J. L. Margrave, and M. S. Newman, *J. Amer. Chem. Soc.*, **87**, 5554 (1965).

[16] In this mechanism, the energy barrier to cyclization occurs along the pathway from **2*** to **15***.

[17] Based on theoretical calculations by A. Warshel and A. Bromberg, *J. Chem. Phys.*, **52**, 1262 (1970).

[18] Schemes II, III, and V should be analogously augmented to include skewed dihydrophenanthrene intermediates.

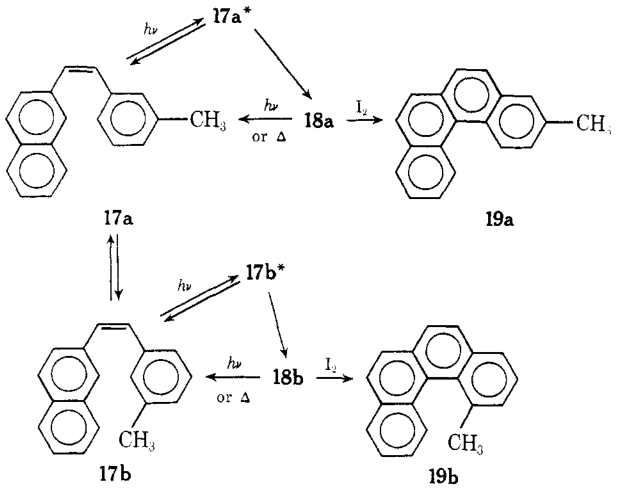
Scheme IV



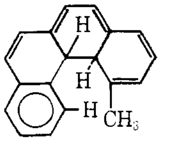
and **16b*** that would be diverted back to **12a** and **12b**, respectively.

We have studied the photocyclization of *cis*-2-(*m*-methylstyryl)naphthalene (**17**) as a further example of a system involving the analogous kind of steric requirements found in *cis*-*m*,*m*′-dimethylstilbene. There are four ground-state conformers in this system, each of which as a first approximation would comprise 25% of the sample in solution; but only two of these, **17a** and **17b**, need to be considered here (see Scheme V),[9] since the observed photocyclization products consist almost exclusively of the benzo[*c*]phenanthrenes **19a** and **19b**, together with only traces of the benz[*a*]anthracenes derived from the other two conformers of **17**. On the basis of the well-established generalization that a fused benzene ring is sterically comparable to a methyl group,[15] the photocyclization behavior for **17a** and **17b** should be very similar to that observed for **12b** and **12c** (except that the statistical factor of 2 associated with **12b** does not apply to **17a**). In fact, the **19a**/**19b** product ratio was found to be 61/39 = 1.56 (see Table I), which is in good agreement with the statistically corrected **14b**/**14c** product ratio of 54(0.5)/18 = 1.50. We take this agreement as support for our interpretation of the photocyclizations in these two systems in terms of steric effects involving the interior meta and meta′ substituents.

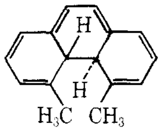
Scheme V



The **19a**/**19b** product ratio was found to have the same value, 1.56, for concentrations of iodine varying from 5 × 10^{-4} to 5 × 10^{-2} *M*; this is in striking contrast to the behavior of the **14b**/**14c** ratio, which was found to decrease from 7.9 to 1.50 (statistically corrected) over this range of iodine concentrations (Table I). This implies that the thermal ring opening of the dihydro intermediate **18b** does not compete effectively with the oxidative trapping of this intermediate to give **19b**, in spite of the fact that the steric strain in **18b** should be comparable, according to the generalization cited above,[15] to that in **13c**. This apparent anomaly is readily explained by noting that in the **13c** → **12c** ring opening, the resonance stabilization of two benzene rings is gained, whereas in the **18b** → **17b** reaction only the resonance stabilization of one benzene ring plus the difference in resonance stabilization between a naphthalene system and a benzene ring is gained. One can use either the traditional resonance energy values (benzene, 36.4 kcal/mol; naphthalene, 61.2 kcal/mol)[19a] or some more recently advocated values (benzene, 22.6 kcal/mol; naphthalene, 33.6 kcal/mol)[19b] to estimate that the **18b** → **17b** transformation is about 11.6 kcal/mol less exothermic than the **13c** → **12c** transformation. Therefore, one expects[20] a slower rate for **18b** → **17b** than for **13c** → **12c**, with the consequence that oxidative trapping of **18b** is easier than that of **13c**.



18b



13c

A number of other meta-substituted stilbenes have been irradiated for preparative purposes by ourselves and others, and the results are consistent with those obtained in the detailed studies reported above. In some cases approximately equal amounts of the two products were isolated, while in other cases a slight deficiency of the 4-substituted phenanthrene was obtained, presumably because of the selective photodecomposition of this isomer that can become significant when the reactions are carried to completion by prolonged irradiation. The compounds studied in this way include *m*-methoxystilbene, *m*-fluorostilbene, *m*-phenylstilbene,[21] 2-(*m*-methylstyryl)thiophene,[22] a series of *m*-fluorostilbenes with various ortho′ or para′ substituents,[23] and a series of *o*- and *p*-fluorostilbenes having a meta′ substituent such as fluoro, chloro, bromo, methyl, or methoxy.[23]

In one of the pioneering studies of stilbene photocyclization,[24] the irradiation (without iodine) of *m*,*m*′-dimethoxystilbene was found to give a mixture of 2,7-dimethoxyphenanthrene (**20a**) and 2,5-dimethoxyphenanthrene (**20b**) with an overall yield of 73% and a **20a**/**20b** ratio of 1.6; no 4,5-dimethoxyphenanthrene (**20c**) was detected. By analogy with our present results for the dimethyl system (**12**), we suggest that the absence of **20c** in the dimethoxy product mixture was mostly a consequence of the inefficiency of oxygen in trapping the dihydrophenanthrene precursor. The surprisingly high **20a**/**20b** ratio (as compared to the ratio of 0.52 for the corresponding dimethyl compounds **14a** and **14b**, for example) may have been due, in part, to the selective destruction of **20b** under the reaction

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(24) P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960).

conditions. A similar explanation presumably accounts for the very high value of 3:1 reported[25] for the ratio of 2- to 4-hydroxyphenanthrene produced by the irradiation of *m*-hydroxystilbene.

Experimental Section

Melting points were measured in an oil bath and are uncorrected. Analyses by gas–liquid chromatography (glc) were accomplished with an F & M Model 400 gas chromatograph equipped with a flame ionization detector, a Disc integrator, and (except as noted) the column described in footnote *a* of Table I. Ultraviolet absorption spectra were obtained with a Cary Model 14 spectrophotometer. Unless otherwise specified, Merck 71707 alumina was used for column chromatography. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Preparative irradiations were carried out in a water-cooled, custom-made immersion apparatus with a quartz well. The light source was an unfiltered 100-W General Electric H100A4/T mercury lamp, modified as described elsewhere.[26] Magnetically stirred solutions of the stilbene in redistilled Eastman practical grade cyclohexane were irradiated until the reactions were judged complete by glc. The crude product mixtures were isolated by removal of the cyclohexane under reduced pressure with a rotary evaporator.

trans-m-**Methylstilbene.** Dehydration with refluxing dilute aqueous sulfuric acid of the carbinol resulting from the reaction of *m*-tolylmagnesium bromide with phenylacetaldehyde followed by purification of the crude product by vacuum distillation and three recrystallizations from 95% ethanol gave *trans-m*-methylstilbene, mp 48.4–49.0° (lit.[27] mp 48°).

trans-m,m'-**Dimethylstilbene.** Perkin condensation[28] of *m*-tolylacetic acid with *m*-tolualdehyde was followed by decarboxylation of the resulting 2,3-di-*m*-tolylacrylic acid with copper chromite catalyst in quinoline.[29] The material thus produced was subjected to iodine-catalyzed thermal isomerization, column chromatography with 60–70° ligroin as eluent, and two recrystallizations from methanol to give *trans-m,m'*-dimethylstilbene, mp 58.0–59.0° (lit.[30] mp 55–56°).

Methyl- and Dimethylphenanthrenes. The products from the irradiation of *trans-m*-methylstilbene were identified as 2- and 4-methylphenanthrene (**7a** and **7b**, respectively) and those from the irradiation of *trans-m,m'*-dimethylstilbene were identified as 2,7-, 2,5-, and 4,5-dimethylphenanthrene (**14a**, **14b**, and **14c**, respectively) by comparisons of their glc retention times on two different columns with those reported by Solo and Pelletier.[31] The columns used were the previously specified neopentyl glycol succinate column maintained at 181° and a 1.2 m × 6 mm glass column packed with 3.8% SE-30 on 80–100 mesh Gas Chrom S maintained at 141°. Authentic samples of phenanthrene, 1-methylphenanthrene, and 3-methylphenanthrene were also analyzed to confirm that our measured retention times corresponded to those found by the other workers;[31] the agreement was within 1% in all cases.

To allow further characterization of 4,5-dimethylphenanthrene, it was isolated from an irradiation of 210 mg (1 mmol) of *trans-m,m'*-dimethylstilbene in 200 ml of cyclohexane containing 1.27 g (5 mmol) of iodine ($2.5 \times 10^{-2}\ M$). The crude product mixture was chromatographed, first on alumina and then on silicic acid, with petroleum ether and benzene-petroleum ether mixtures as eluents. A fraction was thereby obtained in which about 90% of the material had the glc retention time of 4,5-dimethylphenanthrene. The ultraviolet absorption spectrum of this fraction confirmed our identification, since it exhibited all of the characteristic features that have been reported[32] for the rather structured spectrum of 4,5-dimethylphenanthrene.

trans-m-**Chlorostilbene.** The product of the Grignard reaction of benzylmagnesium chloride and *m*-chlorobenzaldehyde was dehydrated with aqueous sulfuric acid and the resulting material was purified by vacuum distillation and recrystallization from 95% ethanol to give *trans-m*-chlorostilbene, mp 73.0–73.8° (lit.[33] mp 74°).

2- and 4-Chlorophenanthrene. A solution of 640 mg (3 mmol) of *trans-m*-chlorostilbene and 38 mg (0.15 mmol) of iodine in 300 ml of cyclohexane was irradiated for 9 hr. The crude products were dissolved in a minimum amount of petroleum ether (30–40°) and chromatographed on alumina with the same solvent as eluent. The first-eluted component (which also had the shorter glc retention time) was recrystallized from methanol to give white needles of 4-chlorophenanthrene (**10b**), mp 58.0–58.9° (lit.[34] mp 58.5–59.0°).

In a separate experiment, a solution of 640 mg (3 mmol) of *trans-m*-chlorostilbene in 250 ml of cyclohexane (without iodine) was irradiated for 9 hr with a 400-W General Electric mercury lamp. The ratio of 2- to 4-chlorophenanthrene in the crude product was shown by glc to be about 2:1. The reaction mixture was poured through an alumina column, and a 1:1 mixture of benzene and ligroin (60–70°) was used to elute all nonresinous material. The solvents were evaporated under reduced pressure and the residue was chromatographed on alumina with ligroin as eluent. The combined material from those fractions shown by glc to contain predominantly the component with the longer retention time was recrystallized from 95% ethanol to give white crystals of 2-chlorophenanthrene (**10a**), mp 82.0–85.0° (lit.[35] mp 85.5–86.0°).

trans-m-**Trifluoromethylstilbene and 2- and 4-Trifluoromethylphenanthrene.** The synthesis, separation, and characterization of each of these compounds has been described elsewhere.[36]

trans-**2-(*m*-Methylstyryl)naphthalene.** A similar procedure to that described above for *trans-m,m'*-dimethylstilbene was used to convert 2-naphthylacetic acid and *m*-tolualdehyde into *trans*-2-(*m*-methylstyryl)naphthalene. Purification of this product by chromatography on alumina with ligroin as eluent, two recrystallizations from 95% ethanol, and a final sublimation gave material with mp 126.8–127.4°.

Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.34; H, 6.69.

1- and 3-Methylbenzo[*c*]phenanthrene. A solution of 488 mg (2 mmol) of *trans*-2-(*m*-methylstyryl)naphthalene and 25 mg (0.1 mmol) of iodine in 300 ml of cyclohexane was irradiated for 6 hr. Quantitative glc analysis with the starting material as an added internal standard indicated a product composition of 35% 1-methylbenzo[*c*]phenanthrene (the shorter retention time component) and 65% 3-methylbenzo[*c*]phenanthrene (longer retention time), and a total yield of 81%. The crude products were chromatographed on alumina with petroleum ether (30–60°) as eluent. The eluted material was recrystallized from methanol to give 1-methylbenzo[*c*]phenanthrene (**19b**), mp 139.1–141.0° (lit.[37] mp 141.4–141.9°). This material failed to form a picrate derivative, as has been previously reported[37] for 1-methylbenzo[*c*]phenanthrene.[38] Further elution of the alumina column with a 3:1 mixture of ligroin and benzene gave 3-methylbenzo[*c*]phenanthrene (**19a**) as an oil. The picrate derivative was prepared and recrystallized twice from 95% ethanol to give material with mp 134.8–135.2° (lit.[39] mp 134.0–134.5°). The hydrocarbon was regenerated from this picrate by chromatography on alumina with a 1:1 mixture of ligroin and benzene. Evaporation of the solvents under reduced pressure and recrystallization of the residue from methanol gave 3-methylbenzo[*c*]phenanthrene (**19a**), mp 52.0–54.4° (lit.[39] mp 54.0–54.5°). The ultraviolet absorption spectra of 95% ethanol solutions of the samples of **19a** and **19b** obtained in this work were in excellent agreement with the data previously presented for these compounds.[40]

trans-m-**Methoxystilbene.** From the reaction of benzylmagnesium chloride with *m*-anisaldehyde, followed by acid-induced dehydration and vacuum distillation, there was obtained *trans-m*-methoxystilbene, mp 21–23° (lit.[41] mp 21–24°).

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(38) All other monomethyl benzo[*c*]phenanthrenes, as well as all monomethyl benz[*a*]anthracenes, form picrates in the normal way; see M. Orchin, *J. Org. Chem.*, **16**, 1165 (1951).

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(41) G. A. R. Kon and R. G. W. Spickett, *ibid.*, 2724 (1949).

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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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$_6$D$_6$) or C$_6$D$_6$–C$_6$H$_6$ 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).

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

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