fluence on complexing must be negligible. With ring deuteration only and no alkyl substituents, it is unlikely that any hyperconjugative effect is present which would act in the opposite direction.[29]

On the difference in isotope effect between diene and dienophile, we would like to suggest that this represents only a different degree in hybridization change at the transition state for the diene relative to the dienophile. In other words, the bonding in the diene appears to change without a complementary change in the dienophile. At this point we would prefer not to speculate on what kind of transition-state structures could accommodate this observation.

The third feature of our data, the increase in isotope effect in proceeding from butadiene to cyclopentadiene to anthracene, is the most difficult to rationalize. Fundamentally this indicates that the amount of hybridization change of the dienophile (maleic anhydride) in going from reactant to transition state is dependent on the diene under attack. This obviously does not parallel the reactivity of the diene which is cyclopentadiene > butadiene > anthracene. A parallelism of isotope effect to the entropy of activation of each reaction seems to exist (more negative ΔS^* corresponds to lower k_D/k_H), but lack of precision in the data of

(29) E. A. Halevi and M. Nussim, J. Chem. Soc., 876 (1963).

kinetic parameters for these reactions excludes a quantitative correlation.

In conclusion, the isotope effects observed in the forward Diels–Alder reaction are consistent with a one-step mechanism which is the microscopic reverse of that observed in the retro reaction.[12] In the forward reaction, the amount of bond formation is small with the transition state lying only a short distance along the reaction coordinate from the reactants. While the transition state need not be completely symmetrical and may involve differences in degree of hybridization change between diene and dienophile, the reaction can still be formally classed as four centered. The sensitivity of the isotope effect to moderate deuterium positional and structural changes in the reactants emphasizes the difficulties attendant in calculating an "expected" effect from the appropriate statistical mechanical equations and assumed values for vibration frequencies, or, more fundamentally, bond force constants of transition states.

Photochemistry of Stilbenes. III. Some Aspects of the Mechanism of Photocyclization to Phenanthrenes[1,2]

BY FRANK B. MALLORY,[3] CLELIA S. WOOD, AND JANICE T. GORDON

With certain exceptions, stilbene derivatives are converted photochemically in good yields to the corresponding phenanthrene derivatives in cyclohexane solution in the presence of oxidants such as dissolved oxygen or iodine. The scope and mechanism of this photoreaction are discussed in detail. The mechanism is believed to involve cyclization of cis-stilbene in its lowest excited singlet state to give an unorthodox dihydrophenanthrene which then undergoes hydrogen abstraction by the oxidant to give phenanthrene. The differences between the course of the photoreaction of stilbene in the vapor phase and in solution are discussed.

Introduction

Irradiation with ultraviolet light of solutions containing cis-stilbene in the presence of a suitable oxidant such as dissolved molecular oxygen has been found to lead to the formation of phenanthrene in good yield.[4] This photoreaction of stilbene or certain substituted stilbenes has also been discovered independently by several other workers,[5] and some limited studies have been carried out.[6] In some of these previous reports

(1) Part II: F. B. Mallory, J. T. Gordon, and C. S. Wood, J. Am. Chem. Soc., **85**, 828 (1963).

(2) Taken in part from the Ph.D. Dissertations of (a) C. S. Wood, Bryn Mawr College, 1963, and (b) J. T. Gordon, Bryn Mawr College, 1961.

(3) John Simon Guggenheim Memorial Foundation Fellow 1963–1964.

(4) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, J. Am. Chem. Soc., **84**, 4361 (1962).

(5) (a) C. O. Parker and P. E. Spoerri, Nature, **166**, 603 (1950); (b) R. E. Buckles, J. Am. Chem. Soc., **77**, 1040 (1955); (c) D. G. Coe, E. W. Garnish, M. M. Gale, and C. J. Timmons, Chem. Ind. (London), 665 (1957); (d) E. A. Rick, Ph.D. Thesis, Yale University, 1959; (e) E. J. Moriconi, private communication, (f) G. W. Griffin, private communication; (g) D. H. R. Barton, private communication.

(6) (a) P. Hugelshofer, J. Kalvoda, and K. Schaffner, Helv. Chim. Acta, **43**, 1322 (1960); (b) C. R. Evanega, private communication; (c) H. Stegemeyer, Z. Naturforsch., **17b**, 153 (1962); (d) R. Srinivasan and J. C. Powers, Jr., J. Am. Chem. Soc., **85**, 1355 (1963); (e) J. Chem. Phys., **39**,

the need for an oxidant was not appreciated and the formation of the phenanthrene occurred as a result of the adventitious presence of dissolved oxygen or other oxidants.[5a,b,6c] In other early reports the identity of the photoproduct was not established as phenanthrene.[7]

As postulated earlier,[4] the reaction is believed to involve as an intermediate the unorthodox dihydrophenanthrene[8] shown below. The postulation of this inter-
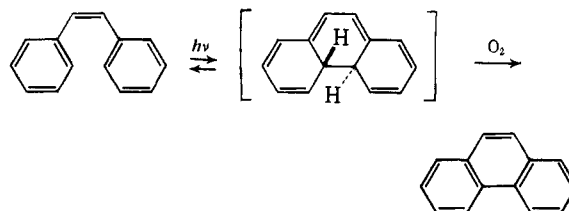
580 (1963); (f) M. V. Sargent and C. J. Timmons, J. Am. Chem. Soc., **85**, 2186 (1963).

(7) (a) A. Smakula, Z. physik. Chem., **B25**, 90 (1934); (b) G. N. Lewis, T. T. Magel, and D. Lipkin, J. Am. Chem. Soc., **62**, 2973 (1940); (c) G. Oster, G. K. Oster, and H. Moroson, J. Polymer Sci., **34**, 671 (1959).

(8) Throughout this paper the name "dihydrophenanthrene" will be used to designate the 4a,4b-dihydrophenanthrene shown above unless specified to the contrary.

mediate makes the over-all removal of two hydrogens in the conversion of stilbene to phenanthrene readily understandable since the two tertiary and doubly allylic hydrogens of the dihydrophenanthrene should be very susceptible to abstraction by a suitable oxidant. Similar intermediates have been postulated independently for related reactions.[5d,6a,9]

We have shown that irradiation of stilbene in cyclohexane solution under a nitrogen atmosphere with careful exclusion of oxygen fails to produce phenanthrene at a detectable rate.[10] This result has been confirmed in other laboratories.[5d,6d,6e,12] Under these conditions photochemical cis–trans isomerization of stilbene takes place with essentially no net loss in the total amount of stilbene.[13] Thus, it is suggested[4] that the dihydrophenanthrene must undergo ring opening under the irradiation conditions to regenerate cis-stilbene at such a rate that the steady-state concentration of this intermediate is low relative to the concentration of stilbene.

Since our first preliminary report, evidence has been presented which strongly indicates the existence of a dihydrophenanthrene intermediate such as that postulated above.[12,14] The thermal ring opening of the dihydrophenanthrene has been found[14] to occur with a half-life on the order of 2 hr. at 30°. It has also been found that this ring opening can be accomplished photochemically.[14–16]

Our first efforts were directed toward developing the reaction into a useful synthetic method for the preparation of substituted phenanthrenes. The results of these efforts will be discussed only briefly here; this aspect of the work will be considered in detail in a subsequent publication.

Dissolved oxygen was the oxidant found to be most convenient for irradiations carried out on a small scale in dilute solution (2–3 ml. of ca. 10^{-5} M solution in a 1-cm. quartz spectrophotometer cell using an externally mounted mercury arc); under these conditions the total amount of stilbene to be converted is small and the photoreaction can be completed in irradiation times on the order of minutes with nearly quantitative yields of phenanthrene as determined spectrally. However, for preparative-scale work (500–1000 ml. of ca. 10^{-2} M solution using an internally mounted mercury arc) it was found to be undesirable to use oxygen as the oxidant; irradiation times on the order of days may be required for conversion of gram quantities of stilbene, and all of the different solvents which were tried[17] underwent extensive photooxidation under these conditions with the formation of tars which seriously inter-

fered with the absorption of light by the stilbene and hence led to incomplete conversions. Among the other oxidants which were tried, chloranil and selenium were found to be effective although not without experimental drawbacks; sulfur, tellurium, selenium dioxide, and palladium-on-carbon were found not to be successful as oxidants.

The most satisfactory conditions found for preparative-scale conversions involve the use of a combination of two oxidants, oxygen and iodine, in cyclohexane solution.[18] For example, for a reaction starting with 0.01 mole (1.8 g.) of stilbene the best results were obtained using 0.0005 mole of iodine[19] in 1 l. of cyclohexane under an air atmosphere; under these conditions the conversion of the stilbene was complete after about 7 hr. of irradiation with a 100-watt mercury arc, and an 82% yield of phenanthrene was obtained after purification by chromatography and sublimation.[21] The presence of the small amount of iodine specified above (5×10^{-4} M) increases the rate of conversion of the stilbene by about a factor of ten compared to the rate in the presence of the oxygen alone (2×10^{-3} M in air-saturated cyclohexane[22]). When the conditions described above are modified by maintaining a nitrogen atmosphere and excluding dissolved oxygen so that iodine is the only oxidant present, the time required for complete conversion of the stilbene is not altered significantly, although the yield and the purity of the phenanthrene are both somewhat decreased. We presume that hydrogen iodide is produced during these irradiations.[23] This presumption implies that iodine must be regenerated from the hydrogen iodide under the irradiation conditions, since the iodine color does not markedly fade during the irradiation and since the conversion of the stilbene is complete in the presence of only five mole per cent of iodine (based on stilbene); this regeneration could be accomplished by photolysis and also by oxidation with oxygen.

Scope of the Reaction.—The photoconversion of substituted stilbenes to the corresponding phenanthrenes in the presence of small amounts of iodine in air-saturated cyclohexane solution has been found to be a reaction of wide scope with yields generally in the 60–85% range on a scale of 2–3 g. Successful conversions have been achieved with stilbenes bearing the substituents: fluoro, chloro, bromo, methoxyl, methyl, trifluoromethyl, phenyl, and carboxyl.[24] The reaction fails to take place with stilbenes having nitro, acetyl, or dimethylamino substituents. Iodo substituents are lost owing to the facile photolysis of carbon–iodine bonds[26] thus

(9) H. Brockmann and R. Mühlmann, Ber., **82**, 348 (1949).

(10) It seems likely, therefore, that oxygen or some other oxidant was inadvertantly present in the two cases reported recently of the photochemical formation of phenanthrene systems under a nitrogen atmosphere.[6a,11]

(11) G. J. Fonken, Chem. Ind. (London), 1327 (1962).

(12) W. M. Moore, D. D. Morgan, and F. R. Stermitz, J. Am. Chem. Soc. **85**, 829 (1963).

(13) Photodimerization to tetraphenylcyclobutane is negligible[2] if the total stilbene concentration is less than about 10^{-2} M.

(14) J. Saltiel, Ph.D. Thesis, California Institute of Technology, 1964; 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, J. Am. Chem. Soc., in press.

(15) W. M. Moore, private communication.

(16) The importance of photochemical ring opening of the dihydrophenanthrene was underestimated earlier.[4]

(17) Solvents tried included cyclohexane, benzene, ethanol, acetic acid, chlorobenzene, dimethylformamide, and dimethyl sulfoxide. Some perfluorinated solvents kindly supplied by the Minnesota Mining and Manufacturing Co. were not useful owing to the low solubility of stilbene in these solvents.

(18) Benzene is useful as a solvent in which to carry out the irradiation of certain stilbenes which are insufficiently soluble in cyclohexane.

(19) Since there are several conceivable modes by which iodine might be expected to act as a quencher for the photocyclization reaction, it was surprising that the rate of production of phenanthrene under these preparative-scale conditions was found not to be significantly affected by varying the amount of iodine used from 0.0005 mole up to 0.01 mole.[20]

(20) C. S. Wood, unpublished results.

(21) F. B. Mallory, J. Chem. Educ., **39**, 261 (1962).

(22) J. E. Jolley and J. H. Hildebrand, J. Am. Chem. Soc., **80**, 1050 (1958).

(23) An acidic gas believed to be hydrogen iodide was detected as a product of the irradiations using iodine under a nitrogen atmosphere.

(24) This type of photocyclization has also been observed using dissolved oxygen as the oxidant with stilbene derivatives having the above-mentioned substituents and also with those having hydroxyl[6a,25] and cyano[6f] substituents.

(25) H. Brockmann and H. Eggers, Angew. Chem., **67**, 706 (1955).

(26) N. Kharasch and W. Wolf, J. Org. Chem., **26**, 283 (1961); N. Kharasch, W. Wolf, T. J. Erpelding, P. G. Naylor, and L. Tokes, Chem. Ind. (London), 1720 (1962).

p-iodostilbene gives phenanthrene[2a] and α,α'-diiodo-stilbene gives diphenylacetylene.[2a]

The irradiation of *o*-, *p*-, or α-substituted stilbenes leads to the formation of 1-, 3-, or 9-substituted phenanthrenes, respectively. Mixtures of comparable amounts of 2- and 4-substituted phenanthrenes are obtained from the irradiation of *m*-substituted stilbenes.[2,6a] α-Styrylnaphthalene is converted photochemically to chrysene.[2a,6a]
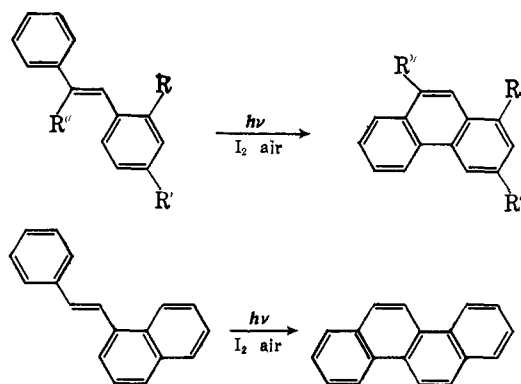

The photocyclization of stilbenes to dihydrophenanthrenes can be considered formally to be a special case of a general reaction of which the conversion of *cis*-1,3,5-hexatriene to 1,3-cyclohexadiene is perhaps the simplest example.[27] Similar photocyclizations of
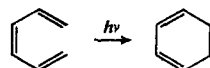
conjugated aliphatic trienes are known to occur with certain compounds related to vitamin D[28] and also with some simply substituted trienes.[29] It is reasonable that the cyclohexadienes formed in this way are apparently not aromatized to benzene derivatives with the great facility that the dihydrophenanthrenes formed from stilbenes are aromatized to phenanthrenes.

Examples of this general reaction are also known in which only one of the terminal unsaturated linkages is incorporated into an aromatic system. In these cases the reactions are believed to proceed by way of photocyclization to dihydronaphthalene intermediates which are rapidly dehydrogenated by dissolved oxygen. Thus 1,4-diphenylbutadiene gives 1-phenylnaphthalene[11] and dibenzalsuccinic anhydride gives 1-phenylnaphthalene-2,3-dicarboxylic acid anhydride.[30,31]
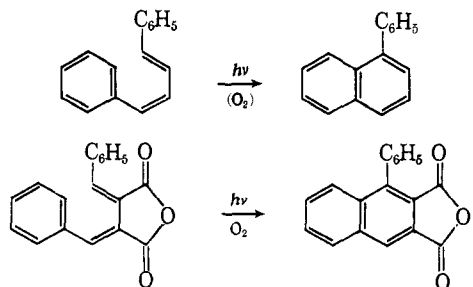

(27) R. Srinivasan, *J. Chem. Phys.*, **38**, 1039 (1963).

(28) (a) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, Chapter 4; (b) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961).

(29) G. J. Fonken, *Tetrahedron Letters*, 549 (1962).

(30) H. Stobbe, *Ber.*, **40**, 3372 (1907); for other examples see F. G. Baddar, L. S. El-Assal, and M. Gindy, *J. Chem. Soc.*, 1270 (1948).

Incorporation of the central unsaturated linkage of a conjugated triene into an aromatic system apparently precludes photocyclization of the type under discussion (although one exception has been reported). Thus, *o*-terphenyl does not undergo oxidative photocyclization to give triphenylene. Also, tetraphenylethylene is converted photochemically to 9,10-diphenylphenanthrene and a second ring closure does not occur even on prolonged irradiation.[2a,5d] Similarly, the compounds with X = O and X = S as indicated below undergo only a

dibenzotriphenylene
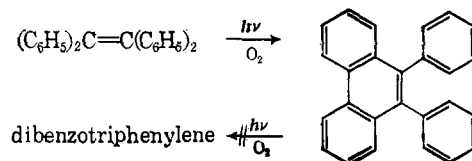
single photocyclization.[32] A possible interpretation of
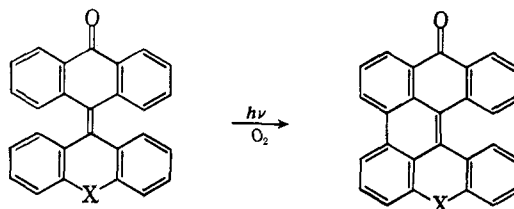
this apparent requirement that the central unsaturation be olefinic for photocyclization to occur is that without this structural feature the electronic distribution in the excited state may be such that there is not sufficient electron availability at the two *ortho* positions between which the new bond would be expected to form. For example, in 9,10-diphenylphenanthrene the excitation in the excited singlet state[33] is probably confined largely to the phenanthrene system with little involvement of the two phenyl groups; this notion is supported by the fact that the ultraviolet absorption spectrum of 9,10-diphenylphenanthrene bears a strong resemblance to that of phenanthrene and is not closely similar to that of *cis*-stilbene. The exception to this behavior is in the bianthrone system (X = CO); thus, both bianthrone itself[9] and a substituted bianthrone[25] have been reported to undergo two successive oxidative photocyclizations to give naphthodianthrones. The reasons for this anomalous character of bianthrones are not known at present.

Mechanism of the Reaction.—For the mechanistic discussion to follow it is necessary to consider the relative energies of the various species which may be produced following the absorption of a photon by either of the stilbenes. A diagram of these energies[34] is shown in Fig. 1.

One of the most pertinent energies in the diagram is that of the proposed dihydrophenanthrene intermediate in its ground state relative to the energy of ground-state *cis*-stilbene. This quantity has not been measured ex-

(31) It should be noted that aromatization by way of elimination of molecular hydrogen without the intervention of an oxidant has been reported to occur in the vapor-phase photocyclizations of 1,3,5-hexatriene,[27] 1,4-diphenylbutadiene,[he] and stilbene.[6d,e] This type of aromatization appears to be quite rigorously excluded in the condensed-phase irradiations of these molecules.

(32) (a) A. Schonberg, A. F. A. Ismail, and W. Asker, *J. Chem. Soc.*, 442 (1946); (b) A. F. A. Ismail and Z. M. El-Shafel, *ibid.*, 3393 (1957).

(33) It will be argued later in the present paper that singlet-state rather than triplet-state molecules are involved in the ring closure.

(34) In this discussion energies and enthalpies will be considered equal in magnitude.

perimentally, but it can be estimated approximately by a Hess' law summation over the following hypothetical pathway (not to be confused with a mechanism) involving four imaginary species *not stabilized by resonance* (*i.e.*, species with *localized* double bonds or unpaired electrons).
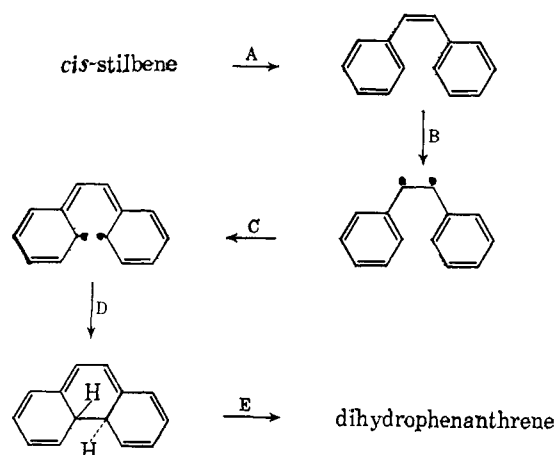
Step A is endothermic by the magnitude of the resonance energy of *cis*-stilbene. It is known from heat of hydrogenation measurements[35] that *cis*-stilbene differs in enthalpy from *trans*-stilbene by 5.7 kcal./mole. The hypothetical Kekulé structures with noninteracting double bonds which would be used as standards for calculating the resonance energies of the two stilbenes are expected to differ from one another by only 1 kcal./mole by analogy with a variety of *cis–trans* pairs of dialkylethylenes which are known[36] to differ by about this amount. Thus, the resonance energy of *cis*-stilbene is taken to be 4.7 kcal./mole less than that of *trans*-stilbene. Eight different estimates of this latter quantity ranging from 75.5 to 78.0 kcal./mole can be obtained[36,37] from various experimental heats of combustion and heats of hydrogenation; using the average of these values, 76.8 kcal./mole, the resonance energy of *cis*-stilbene is found to be 72.1 kcal./mole.

The endothermicity of step B is estimated to be 55.4 kcal./mole by analogy with the enthalpies which can be calculated for the corresponding opening of the π-bond in various model olefins from appropriate heats of formation[36a] and bond dissociation energies.[38] For example

		ΔH, kcal./mole
cis-3-hexene $\longrightarrow$ 6C + 6H$_2$		11.6
6C + 7H$_2$ $\longrightarrow$ *n*-hexane		−40.0
n-hexane $\longrightarrow$ Et–ĊH–ĊH–Et + 2H·		188
2H· $\longrightarrow$ H$_2$		−104.2
cis-3-hexene $\longrightarrow$ Et–ĊH–ĊH–Et		55.4

Similar calculations for *cis*-2-butene, *cis*-2-pentene, and *cis*-2-hexene give values ranging from 55.3 to 55.5 kcal./mole.

(35) R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1395 (1942).

(36) (a) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44," Carnegie Press, Pittsburgh, Pa., 1953; (b) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955; (c) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Am. Chem. Soc.*, **80**, 1430 (1958).

(37) J. Coops and G. J. Hoijtink, *Rec. trav. chim.*, **69**, 358 (1950); J. W. Richardson and G. S. Parks, *J. Am. Chem. Soc.*, **61**, 3543 (1939).

(38) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.
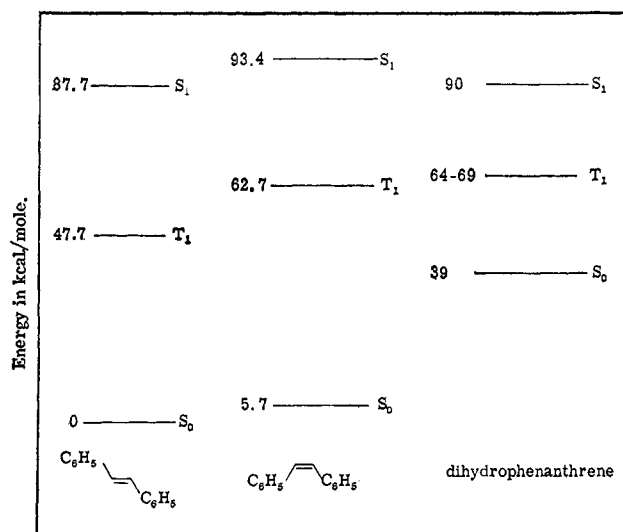
Fig. 1.—Energy level diagram for various electronic states of *trans*-stilbene, *cis*-stilbene, and dihydrophenanthrene.

The similarly calculated enthalpies for opening the π-bond in four different trisubstituted olefins (2-methyl-2-pentene, *cis*- and *trans*-3-methyl-2-pentene, and 2-methyl-2-butene) are all identical (53.1 kcal./mole). Thus, step C, in which two trisubstituted double bonds are opened and two others are closed, is estimated to involve no enthalpy change.

Step D is estimated to be exothermic by 76.7 kcal./mole by analogy with the coupling of two isopropyl radicals[36a,38]

		ΔH, kcal./mole
2(CH$_3$)$_2$CH$_2$	$\longrightarrow$ 6C + 8H$_2$	49.6
6C + 7H$_2$	$\longrightarrow$ (CH$_3$)$_2$CH–CH(CH$_3$)$_2$	−42.5
2(CH$_3$)$_2$CH· + 2H·	$\longrightarrow$ 2(CH$_3$)$_2$CH$_2$	−188
H$_2$	$\longrightarrow$ 2H·	104.2
2(CH$_3$)$_2$CH·	$\longrightarrow$ (CH$_3$)$_2$CH–CH(CH$_3$)$_2$	−76.7

Step E is exothermic by the magnitude of the resonance energy of the dihydrophenanthrene; this quantity is estimated by means of an empirical equation[39] to be 17.5 kcal./mole.

Thus, the over-all conversion of *cis*-stilbene in its ground state (S$_0$) to the dihydrophenanthrene (S$_0$) is calculated to be endothermic by 33.3 kcal./mole; the uncertainty in this figure may be ± 10 kcal./mole.

The assignments of the energies of the lowest excited singlet (S$_1$) and triplet (T$_1$) states in Fig. 1 are based on spectroscopic data. The energy of the O–O band of the S$_0$ → T$_1$ transition for *trans*-stilbene can be estimated to be 47.7 kcal./mole from the absorption spectrum[40] (ethyl iodide enhancement); this same value has been obtained from studies of the photosensitized isomerization of the stilbenes.[14] Similarly, the energy of the O–O band of the S$_0$ → T$_1$ transition for *cis*-stilbene has been estimated to be 57.0 kcal./mole both from the absorption spectrum[41] (high-pressure oxygen enhancement) and from isomerization studies.[14] The triplet excitation energy for the dihydrophenanthrene is roughly guessed to be 25–30 kcal./mole by analogy with other polyolefins.[42] The energy level of the lowest excited singlet state (S$_1$) of *trans*-stilbene has been found

(39) Reference 36b, p. 131.

(40) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(41) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(42) D. F. Evans, *ibid.*, 1735 (1960).

to be 87.7 kcal./mole from both absorption and fluorescence spectra.[40] The analogous energy level of cis-stilbene is known with less certainty; the assignment in Fig. 1 is based on the conclusion that was reached[40] from studies of the absorption spectra of the two stilbenes that the excitation energy of the $S_0 \rightarrow S_1$ transition (O–O band) for cis-stilbene is very nearly equal to the excitation energy of the corresponding transition for trans-stilbene. The absorption spectrum of the dihydrophenanthrene has a very broad band (maximum near 455 mμ[12,14]) which extends to approximately 560 mμ[43]; thus, the energy of the O–O band of the $S_0 \rightarrow S_1$ transition appears to be in the neighborhood of 51 kcal./mole.

Three of the principal mechanistic questions which will be considered here concern whether the photocyclization is one of cis-stilbene, trans-stilbene, or both; whether the cyclization occurs from a singlet-state or a triplet-state stilbene; and whether the intermediate is cis- or trans-4a,4b-dihydrophenanthrene.

Evidence pertinent to the first of these questions is available from other investigations. The initial rate of formation of phenanthrene was found[6c] to be finite when a solution of pure cis-stilbene along with some dissolved oxygen was irradiated with ultraviolet light, but the initial rate was found to be zero when a similar solution of pure trans-stilbene was irradiated; in the latter experiment, phenanthrene began to be formed only after cis-stilbene accumulated in the solution from the photoisomerization of the trans isomer. It has also been observed[14] that the yellow-orange color of the dihydrophenanthrene intermediate develops essentially instantly on the irradiation of a degassed solution of pure cis-stilbene (0.05 M) but develops very slowly on the similar irradiation of pure trans-stilbene; again, the color development in the latter case is associated with the slow accumulation of cis-stilbene produced by photoisomerization. Thus, there is no readily accessible pathway by which trans-stilbene (S_1) can undergo conversion to the dihydrophenanthrene. This conclusion, which was also reached earlier,[12] is in accord with the results of spectroscopic studies[7b,40] which have shown that there is a large thermal barrier to the interconversion of trans-stilbene (S_1) and cis-stilbene (S_1).

With the unfiltered mercury arcs used as light sources in the present work the concentration ratio of cis-stilbene to trans-stilbene is about 2.5 in the photostationary state which is attained in the absence of any oxidant; in those photocyclization reactions in which oxygen is the only oxidant used, this cis/trans ratio of about 2.5 is achieved early and maintained throughout most of the reaction. However, under the optimum preparative-scale conditions described above involving the use of iodine, the observed cis/trans concentration ratio during the irradiation is only approximately 0.01 because the iodine atoms produced by the photolysis of molecular iodine are very effective in catalyzing the conversion of cis-stilbene to the thermodynamically more stable trans isomer. Thus, it may seem difficult to justify the assertion that even under these conditions the photocyclization occurs only as a consequence of $S_0 \rightarrow S_1$ excitation of cis-stilbene. But the point is that it is not the bulk concentration of cis-stilbene that is pertinent here. A simple calculation using Beer's

law shows that for a typical reaction mixture 99.99% of the ultraviolet light effective in causing the photocyclization will be absorbed within about the first 0.2 mm. of the solution through which the light travels. Thus, the effective reaction zone for the stilbene photochemistry is only a very small fraction of the total volume of solution in the reaction vessel. On the other hand, the generation of iodine atoms is expected to take place to significant extent throughout the entire reaction mixture since it is the visible light in the 430–580 mμ region from the unfiltered mercury arcs that is believed to be primarily responsible for the photolysis of the iodine,[44] and the absorbance of the reaction mixture in this wave length range is small. Therefore, it is only in the above-mentioned 0.2-mm. reaction zone that the photoisomerization favoring the cis isomer can compete effectively with the iodine-catalyzed isomerization favoring the trans isomer. The over-all success of iodine atoms over photons in establishing a bulk cis/trans ratio of only 0.01 during the preparative-scale reactions may be largely the result of the fact that the iodine atoms are acting throughout a much greater portion of the reaction mixture than the photons. The cis/trans ratio in the 0.2-mm. reaction zone clearly will exceed 0.01 and may actually approach the ratio found in the absence of iodine.

Evidence exists which allows the firm conclusion that the photocyclization to the dihydrophenanthrene intermediate does not occur by way of triplet-state stilbene molecules. One early[4] although not compelling[45] argument was that the cyclizations are not inhibited by the presence of relatively large concentrations of dissolved oxygen. Convincing evidence that triplet-state stilbene does not undergo cyclization comes from the report[14] that the formation of the dihydrophenanthrene is not observed[46] in experiments in which stilbene (T_1) is produced directly by energy transfer from a wide variety of triplet-state photosensitizer molecules rather than indirectly by irradiation followed by an $S_1 \rightarrow T_1$ intersystem crossing.

The assignments of energy levels to cis-stilbene (T_1) and dihydrophenanthrene (T_1) shown in Fig. 1 are consistent with the observed inability of triplet-state stilbene to undergo ring closure. Such a cyclization would be endothermic (if it were to proceed with spin conservation) and hence would not be expected to be sufficiently fast to compete with the other very rapid processes available to cis-stilbene (T_1).[47]

Although it seems clear that the cyclization is occurring from a singlet-state rather than a triplet-state stilbene, the question remains whether the cyclization occurs directly from cis-stilbene (S_1) or whether internal conversion from cis-stilbene (S_1) to vibrationally excited cis-stilbene in its electronic ground state (S_0)* immediately precedes ring closure. It might be reasoned that cyclization does not take place by way of cis-stilbene (S_0)* on the grounds that the collisional deactivation by the solvent of such a vibrationally excited molecule would be so rapid that no chemical process such as

(43) The authors are indebted to Dr. J. Saltiel for making this spectrum available to them.

(44) I. J. Gardner and R. M. Noyes, J. Am. Chem. Soc., **83**, 2409 (1961); G. A. Salmon and R. M. Noyes, ibid., **84**, 672 (1962).

(45) D. W. Setser, D. W. Placzek, R. J. Cvetanovic, and B. S. Rabinovitch, Can. J. Chem., **40**, 2179 (1962).

(46) The presence of even a small concentration of dihydrophenanthrene is readily detected by the absorption of this intermediate in the region around 455 mμ.[14]

(47) cis-Stilbene (T_1) has been found to be too short-lived even to undergo diffusion-controlled quenching by azulene.[14]

cyclization could compete effectively with the deactivation. This argument that deactivation is generally the only process of appreciable probability that is undergone in condensed phase by a "hot" ground-state molecule which is formed by isoenergetic internal conversion or intersystem crossing from an electronically excited molecule is encountered frequently in photochemical discussions.[48-50] However, at least one exception to this behavior has been considered as possible[14] and it would seem imprudent to deny that other exceptions might exist. Nevertheless, since there is no evidence compelling the postulation of cis-stilbene $(S_0)^*$ as an additional intermediate on the way to the dihydrophenanthrene, we choose on the grounds of simplicity to adopt the tentative working hypothesis that the cyclization takes place directly from cis-stilbene (S_1).

Certain stilbene derivatives, including p-acetylstilbene, 2- and 4-styrylpyridine, benzalaniline,[2a,6a] and azobenzene,[2a,6a,48] have been found not to undergo photoconversion to the corresponding phenanthrene derivatives under the irradiation conditions used in the present work. The lowest excited singlet state of each of these stilbene derivatives is believed to be of the n → π* type. These results are taken to imply that the electronic distributions in these molecules in their lowest n → π* excited states are unfavorable for cyclization. The failure of m- and p-nitrostilbene to undergo the photocyclization reaction could perhaps be explained similarly.

The photocyclization of azobenzene to 9,10-diazaphenanthrene has been reported to occur in ethanol-sulfuric acid solution.[51] It is suggested that under these strongly acidic conditions the species actually undergoing cyclization is a protonated one that has a lowest excited singlet state of the π → π* type rather than the n → π* type. Even if only one of the nitrogens were protonated, it seems likely that the n → π* transition involving the remaining lone pair on the adjacent nitrogen would be raised in energy by the presence of the positive charge on the protonated nitrogen so that the lowest excited singlet state would not be reached by this transition. The observation[6a] that azobenzene is photocyclized in glacial acetic acid solution to which ferric chloride has been added could conceivably be given a similar interpretation by assuming that the ferric chloride or some species derived therefrom interacts as a Lewis acid with one or both sets of lone pair electrons on the nitrogens.

Some preliminary evidence has been reported[14] which suggests that the cyclization may take place to give the dihydrophenanthrene in its first excited singlet state (S_1) which subsequently undergoes deactivation to dihydrophenanthrene (S_0). It can be seen from Fig. 1 that such a cyclization is expected to be exothermic and hence is a reasonable mechanistic pathway. However, the alternative mechanism involving ring closure to give ground-state dihydrophenanthrene in a high vibrational level cannot be ruled out at the present time.

The stereochemistry of the two tertiary hydrogens in

the intermediate dihydrophenanthrene in the solution photochemistry has not been demonstrated experimentally. We suggest[4] tentatively that this intermediate has the trans rather than the cis configuration for two

trans-DHP   **cis-DHP**
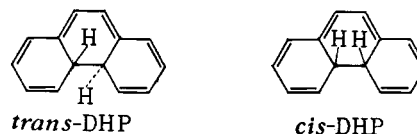
reasons. First, it has been pointed out[52] that photocyclizations of various substituted 1,3,5-hexatrienes related to vitamin D give the corresponding 1,3-cyclohexadienes with the trans configuration at the point of ring closure[53]; in contrast, these same hexatrienes give the cyclohexadienes with the cis configuration when the cyclization is accomplished thermally. Since it is known that the pyrolysis of stilbene gives phenanthrene and hydrogen,[6d,e] a reaction that is most readily formulated as involving a cis type of cyclization,[54] it is tempting to hypothesize that the stilbene system and the hexatriene system are in fact behaving analogously and that the photocyclization, therefore, does take a trans course. This analogy should be viewed cautiously, however, for even though there appear to be similarities between the hexatriene system and the stilbene system, there is also at least one significant difference: the ground-state energy of 1,3-cyclohexadiene can be calculated from appropriate bond and resonance energies [36a,b,38,39] to be about 16 kcal./mole less than that of cis-1,3,5-hexatriene, whereas the ground-state energy of the unorthodox dihydrophenanthrene[55] is calculated as described above to be about 33 kcal./mole greater than that of cis-stilbene.

An example of the potentially treacherous nature of reasoning by analogy in connection with mechanistic questions in excited-state chemistry can be seen by comparing the photocyclization in solution of diphenylamine with that of cis-stilbene. Diphenylamine has been reported[50,56] to photocyclize to an intermediate which was formulated as a dihydrocarbazole of structure closely related to that of the unorthodox dihydrophenanthrene. Furthermore, this intermediate was observed to undergo thermal ring opening to regenerate diphenylamine and also to undergo an aromatization reaction with dissolved oxygen to give carbazole; the similarity of these reactions to those of the dihydrophenanthrene is striking. One might consider diphenylamine to be a modified cis-stilbene in which the σ-bond framework in the vicinity of the central π-electron pair consists of a single nitrogen atom instead of two carbon atoms; that is, the relation between diphenylamine and cis-stilbene could be taken to be simi-

(48) G. Zimmerman, L. Chow, and U. Paik, J. Am. Chem. Soc., **80**, 3528 (1958).

(49) R. Srinivasan, ibid., **85**, 4045 (1963).

(50) H. Linschitz and K.-H. Grellmann, ibid., **86**, 303 (1964).

(51) G. E. Lewis, Tetrahedron Letters, **9**, 12 (1960); J. Org. Chem. **25**, 2193 (1960); G. M. Badger, R. J. Drewer, and G. E. Lewis, Australian J. Chem., **16**, 1042 (1963).

(52) E. Havinga, Photochemistry Symposium, University of Rochester, Rochester, N. Y., March 28, 1963, and private communication.

(53) Another example of this trans type of photocyclization, the conversion of 2,4,6-octatriene to trans-1,2-dimethyl-3,5-cyclohexadiene, has been reported.[29]

(54) It has been suggested[6e] that the thermal reaction of stilbene to give phenanthrene and hydrogen does not involve cis-dihydrophenanthrene as a discrete intermediate but rather is a concerted process. It seems reasonable, however, to presume that the reaction proceeds by way of a configuration approximating the cis-dihydrophenanthrene; whether such a configuration is a high-energy intermediate or merely a transition state cannot be decided on the basis of the available experimental evidence.

(55) The rough calculation of the energy of the dihydrophenanthrene relative to stilbene is not sufficiently elaborate to distinguish between the cis and trans isomers of the proposed intermediate.
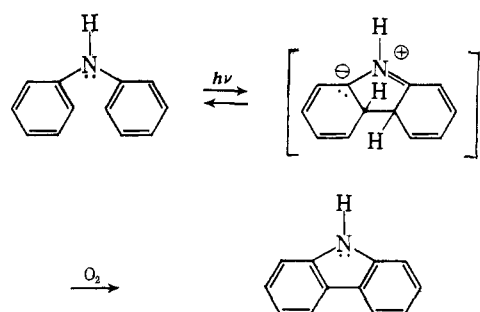
(56) K.-H. Grellmann, G. M. Sherman, and H. Linschitz, J. Am. Chem. Soc., **85**, 1881 (1963).

lar to that between pyrrole and benzene. On the basis of all of these apparent similarities between the two systems, one might be led to speculate that the two photocyclizations are analogous mechanistically. However, this speculation would be grossly incorrect since the photocyclization of diphenylamine has been reported[51] to involve *triplet-state* molecules, and also to involve, in part, elimination *in solution* of molecular hydrogen.[50,57]

A second reason for our current preference for the postulation of *trans*-dihydrophenanthrene rather than *cis*-dihydrophenanthrene as the intermediate is that we find it easier thereby to account for the fact that the photochemical formation of phenanthrene in solution is not detected in the absence of an oxidant. Using the previously described estimate of the relative energy content of the dihydrophenanthrene and appropriate thermochemical data, the conversion of *cis*-dihydrophenanthrene to phenanthrene and hydrogen is estimated to be exothermic by about 47 kcal./mole[55]; the geometry of *cis*-dihydrophenanthrene appears conducive to a *cis* elimination of molecular hydrogen. Under these circumstances, we would anticipate that this elimination reaction would have only a modest activation energy.[58] Cyclization of *cis*-stilbene (S_1) to give, ultimately, dihydrophenanthrene (S_0) is estimated to be exothermic by about 54 kcal./mole. Presumably this exothermicity would manifest itself principally as excess vibrational energy in the dihydrophenanthrene (S_0) which would be transferred collisionally to the solvent.[59] This amount of excess vibrational energy is believed to be considerably more than would be needed to surmount the activation energy barrier for hydrogen ejection from *cis*-dihydrophenanthrene. Even though collisional deactivation of such a vibrationally excited molecule in solution should be very fast, it is conceivable that if the cyclization gave *cis*-dihydrophenanthrene then perhaps a detectable fraction of these "hot" intermediates would give phenanthrene and hydrogen. Thus, the absence of such a reaction indirectly supports our leanings toward considering the intermediate in solution to be *trans*-dihydrophenanthrene.

Clearly neither of the two arguments given in favor of *trans*-dihydrophenanthrene is sufficiently powerful to rule out the possibility that the interme-

(57) E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc.*, 202 (1963).

(58) It has been argued[6d] that hydrogen ejection from *cis*-dihydrophenanthrene may have an activation energy as high as 59 kcal./mole by analogy with the known activation energy for the thermal reaction of cyclopentene to give cyclopentadiene and hydrogen. However, this latter reaction is *endothermic* by 24 kcal./mole[35] and would therefore be expected to have a vastly greater activation energy than the reaction of *cis*-dihydrophenanthrene to give phenanthrene and hydrogen which is estimated as mentioned above to be *exothermic* by about 47 kcal./mole.

(59) The dihydrophenanthrene (S_0) is expected to be formed initially in a high vibrational level, whether it is formed directly from *cis*-stilbene (S_1) or by internal conversion from dihydrophenanthrene (S_1).

diate is actually *cis*-dihydrophenanthrene. It is also easily conceivable that both *cis*- and *trans*-dihydrophenanthrene are produced as intermediates in solution.

After the dihydrophenanthrene intermediate has come to thermal equilibrium with its surroundings there are two principal reactions which it is believed to undergo: ring opening to give *cis*-stilbene and reaction with a suitable oxidant to give phenanthrene. The ring opening has been observed as a spontaneous thermal reaction and can also be photochemically induced[12,14]; a third mechanism for ring opening is also conceivable. Evidence has been obtained[14] which has been interpreted to indicate that dihydrophenanthrene (S_0) is a good quencher of *trans*-stilbene (T_1) by an energy-transfer process leading to the formation of dihydrophenanthrene (T_1) and *trans*-stilbene (S_0). It was suggested[14] that dihydrophenanthrene (T_1) is likely to undergo ring opening to give *cis*-stilbene (T_1); this suggestion is in accord with expectations based on the energy levels shown in Fig. 1. Since *cis*-stilbene (T_1) rapidly isomerizes to *trans*-stilbene (T_1), it is seen that the over-all process would consist of the net conversion of dihydrophenanthrene (S_0) to *trans*-stilbene (S_0) catalyzed by *trans*-stilbene (T_1).

The reaction of the dihydrophenanthrene (DHP) with the oxidant is believed to occur by two successive abstractions of the tertiary hydrogens. For example, the reaction with oxygen is considered to take place as

$$HP\cdot + O_2 \longrightarrow phenanthrene + HO_2\cdot$$
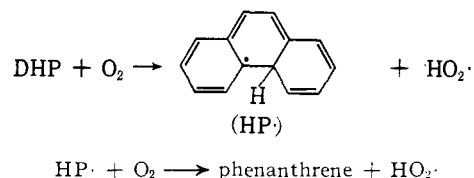
The first abstraction is thought to give rise to a radical, HP·, whose only fate is to undergo a rapid second abstraction to give phenanthrene. This radical, as can be seen by considering another of its resonance forms given below, is one which would be expected to be formed by an intramolecular arylation reaction of the

cis-stilbene radical as shown. Thus, it is anticipated that the HP· radical would not undergo ring opening (the reverse of the process shown above) on the grounds that analogous arylation reactions have been shown[60] to be irreversible. The abstraction by dissolved oxygen of hydrogen atoms from arylation intermediates analogous to HP· has been reported recently.[60b,61] This second hydrogen abstraction could, of course, be effected in a cage reaction between HP· and the HO_2· radical whose formation is postulated in the first abstraction.

In the reaction mixtures used for preparative-scale reactions there are three reagents which could con-

(60) (a) E. L. Eliel, S. Meyerson, Z. Welvart, and S. H. Wilen, *J. Am. Chem. Soc.*, **82**, 2936 (1960); (b) M. Eberhardt and E. L. Eliel, *J. Org. Chem.*, **27**, 2289 (1962).

(61) R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Am. Chem. Soc.*, **84**, 4152 (1962).

ceivably function as hydrogen abstractors: oxygen molecules, iodine molecules, and iodine atoms. The relative efficiencies of these three reagents as hydrogen abstractors are believed to lie in the order $I \cdot > O_2 > I_2$.

The enthalpies for abstracting a particular hydrogen from a molecule should be related to the enthalpies for the combination with a free hydrogen atom, these latter quantities can be calculated from appropriate thermochemical data.[36a,38]

		ΔH, kcal./mole
(a)	$I \cdot + H \cdot \longrightarrow HI$	-71.4
(b)	$H_2O_2 \longrightarrow HO_2 \cdot + H \cdot$	89.5
	$2HO \cdot \longrightarrow H_2O_2$	-52
	$H_2 + O_2 \longrightarrow 2HO \cdot$	20.1
	$2H \cdot \longrightarrow H_2$	-104.2
	$O_2 + H \cdot \longrightarrow HO_2 \cdot$	-46.6
(c)	$I_2 + H \cdot \longrightarrow HI + I \cdot$	-35.3

The endothermicity of the hypothetical reaction in which one of the tertiary hydrogens is lost as a hydrogen atom from the dihydrophenanthrene can be estimated to be roughly 40–45 kcal./mole by a calculative method similar to that described above for obtaining an approximate value for the ground-state energy of dihydrophenanthrene relative to cis-stilbene. The calculation in this case is a crude one and is not considered to be worth describing in detail. The calculated value is of such magnitude that the over-all reaction of dihydrophenanthrene with a particular abstractor to give HP· is estimated to be endothermic with molecular iodine but exothermic with molecular oxygen or with atomic iodine. It is further calculated that the abstraction of hydrogen from HP· to give phenanthrene is far easier energetically than the first abstraction from dihydrophenanthrene. This second abstraction is calculated to be exothermic for molecular iodine as well as for molecular oxygen and atomic iodine.

The existence of a third type of reaction of a dihydrophenanthrene intermediate in addition to ring opening and aromatization has recently been observed. Thus, irradiation of α,α'-dicyanostilbene and diphenylmaleimide in solution in the absence of an oxidant has been reported[6f] to give the two 9,10-dihydrophenanthrenes shown below; these products have been interpreted to arise from isomerization of the unorthodox dihydrophenanthrenes formed by photocyclization. It may be that this type of isomerization is facilitated by the presence of electron-withdrawing
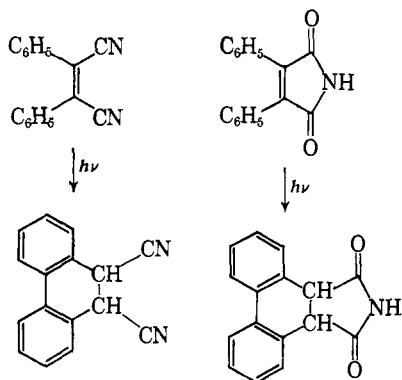
groups at the 9- and 10-positions of the dihydrophenanthrene since we found that no detectable amount of 9,10-dihydrophenanthrene was formed during the

irradiation of stilbene itself in various nitrogen-saturated solvents.[2a,62]

Photoreactions in the Vapor Phase.—It has been reported[6d,e] that the irradiation of cis-stilbene in the vapor phase at 170° gives phenanthrene and an equivalent amount of hydrogen[63] in low quantum yield (ca. 0.003).[64] Although it must be emphasized at the outset that we are not in a position to be able to draw any definite conclusions about the mechanism of this vapor-phase photoreaction, it is not difficult to suggest possible ways of reconciling the sharp contrast between the course of the photoreaction of stilbene in the vapor phase and in condensed phase.[65]

There appears to be no basis for believing that the photocyclization to trans-dihydrophenanthrene should not occur in the vapor phase. At the high temperatures used[6d,e] in the vapor-phase irradiations any trans-dihydrophenanthrene that might be formed would be expected to undergo thermal ring opening rapidly; thus, the fact that the addition of 35 mm. of oxygen to the vapor-phase irradiation was reported not to increase the rate of phenanthrene formation does not necessarily imply that a dihydrophenanthrene intermediate is absent since such an intermediate might be so short lived at 170° that its interception by oxygen would be improbable. In view of the lack of experimental evidence as to the fate of trans-dihydrophenanthrene in the vapor phase at 170° the possibility cannot be excluded that this substance could also undergo conversion to phenanthrene and hydrogen under these conditions. However, the alternative suggestion[6d] that the vapor-phase photoreaction involves cyclization to cis-dihydrophenanthrene as a precursor to phenanthrene and hydrogen appears to have considerable merit.

Since it is known that the thermal reaction of cis-stilbene in the vapor phase gives phenanthrene and hydrogen, a process that almost certainly involves cis-stilbene $(S_0)^*$ as a precursor, it is natural to consider the possibility that this "hot" ground-state molecule may be the species undergoing cyclization and subsequent fragmentation in the vapor-phase photoreaction[66,67]; the suppression of this photoreaction in solution could then be attributed to collisional deactivation of cis-stilbene $(S_0)^*$ by the solvent. The observation[6e] that the addition of up to 704 mm. of diethyl ether vapor did not produce a major quenching

(62) Attempts at catalyzing this isomerization of stilbene by the addition to the irradiation mixtures of p-toluenesulfonic acid, an approach kindly suggested by Professor K. Mislow, were unfortunately unsuccessful.

(63) Under some of the reported conditions the amount of hydrogen detected was less than an eighth of the amount of phenanthrene; it was suggested that hydrogen was being consumed in some way.

(64) This quantum yield is about an order of magnitude lower than the quantum yield for phenanthrene formation in solution in the presence of oxygen as the oxidant.[2a,6c,6e]

(65) Actually it is quite commonplace for molecules to exhibit drastically different photochemical behavior in these two phases. For example, see: G. S. Hammond and N. J. Turro, Science, **142**, 1541 (1963); B. C. Roquitte, J. Am. Chem. Soc., **85**, 3700 (1963); and R. Srinivasan in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 83.

(66) This reaction has been interpreted previously[6e] as arising directly from cis-stilbene (S_1).

(67) The formation of cis-stilbene $(S_0)^*$ from cis-stilbene (S_1) could conceivably occur in at least three ways: (a) internal conversion from S_1; (b) two successive intersystem crossings, $S_1 \rightarrow T_1 \rightarrow S_0^*$; and (c) cyclization to trans-dihydrophenanthrene followed by ring opening. The magnitude of the activation energy barrier for the conversion of cis-stilbene to phenanthrene and hydrogen is not known, but surely process (a) and perhaps even processes (b) and (c) would lead to a cis-stilbene molecule with vibrational energy in excess of that required to surmount this barrier.

effect on the vapor-phase photoreaction could be accounted for if the collision rate required in order for deactivation of cis-stilbene $(S_0)^*$ to be able to compete effectively with cyclization were intermediate between the collision rate in the presence of the added diethyl ether (ca. 10^9 collisions/sec.) and the effective collision rate in solution (ca. 10^{12} collisions/sec.).[68]

Experimental

Preparation of the Light Source.—A 100-watt General Electric H100A4/T mercury lamp was modified by cutting away the outer glass envelope and also by detaching the inner quartz bulb from the screw base on which it was mounted. The two electrical leads from the lamp were then connected by means of insulated wire to a General Electric 9T64Y-3518 or 9T64Y-1019 transformer. The modified mercury lamp was inserted in a 17-mm. i.d. quartz tube that was about 30 cm. long and was sealed on one end.

Preparative-Scale Photoconversion of Stilbene to Phenanthrene.—A mixture of 1.80 g. (0.01 mole) of trans-stilbene (Eastman grade, recrystallized from 95% ethanol, m.p. 123.6–124.2°) and 0.127 g. (0.0005 mole) of iodine was dissolved in 1 l. of cyclohexane (Eastman practical grade, redistilled) in a 1-l. erlenmeyer flask. The flask was placed in a cold water bath consisting of a 10-qt. polyethylene bucket having a drain inserted near the top; the reaction solution was maintained below 33° by running a stream of tap water into the bath. The quartz tube containing the mercury lamp was immersed in the solution that was then magnetically stirred and irradiated for 7 hr.

The reaction mixture was evaporated to dryness under reduced pressure using a rotary evaporator. The residue was dissolved in 50 ml. of warm cyclohexane and the solution was poured onto a column of alumina (Merck 71707) 1.8 cm. in diameter and 6–7 cm. long. The column was eluted with an additional 130 ml. of cyclohexane and the total eluate was evaporated to dryness under reduced pressure. The residue was sublimed[21] to give 1.46 g. (82%) of phenanthrene, m.p. 95–99°. The sublimate was recrystallized from 5 ml. of 95% ethanol to give 1.30 g. (73%) of phenanthrene melting at 98.0–99.4° (lit.[69] m.p. 99.0–99.5°). A small sample that had been exhaustively purified by zone refining melted at 99.4–99.6°.

This general procedure was also used for the photoconversion of various substituted stilbenes to the corresponding phenanthrenes.

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(68) It is being suggested here that the vapor-phase photoreaction of cis-stilbene leading to phenanthrene and hydration involves the cyclization of a considerably shorter-lived species than does the vapor-phase photoreaction of cis-1,3,5-hexatriene leading to benzene and hydrogen, since the latter reaction is quenched quite effectively by added diethyl ether vapor.[27] Two reasons can be advanced to try to make this rate difference seem plausible. First, the preferred geometry of cis-1,3,5-hexatriene is expected to be the s-trans, s-trans conformation that is not suitably disposed for ring closure; this impedance to cyclization is not present in cis-stilbene that is essentially always in an s-cis, s-cis conformation. Second, the activation energy barrier should be considerably larger for the loss of hydrogen from 1,3-cyclohexadiene than from cis-dihydrophenanthrene since the over-all exothermicity is only about 6 kcal./mole for the former reaction compared with about 47 kcal./mole for the latter reaction.

(69) C. C. Price, C. E. Arntzen, and C. Weaver, J. Am. Chem. Soc. **60**, 2837 (1938).

Irradiation of p-Nitrostilbene.—After irradiation for 23 hr. of a solution of 1.13 g. (0.005 mole) of trans-p-nitrostilbene and 38 mg. (0.15 mmole) of iodine dissolved in 700 ml. of cyclohexane, there was recovered following chromatography and sublimation 0.98 g. (87%) of material shown by infrared spectroscopy to be identical with the starting material.

Irradiation of Stilbene under a Nitrogen Atmosphere.—For this type of irradiation a modified form of the reaction vessel described above was used that could be closed off to maintain an inert atmosphere. A solution of 1.80 g. (0.01 mole) of trans-stilbene in 500 ml. of cyclohexane was boiled to expel dissolved oxygen and then cooled under a stream of nitrogen. The vessel was closed and the solution was magnetically stirred and irradiated for 48 hr. A 10-ml. aliquot of the irradiated solution was removed and heated under reflux for 4 hr. with a crystal of iodine to effect the isomerization of the photochemically produced cis-stilbene to the trans isomer.[70] The solvent and the iodine were removed from the aliquot by evaporation under reduced pressure. An infrared spectrum of a carbon tetrachloride solution of the residue gave no evidence for the presence of phenanthrene since there was no detectable peak near 870 cm.[-1]. From this infrared analysis it can be estimated roughly that the rate of formation of phenanthrene in this experiment under a nitrogen atmosphere was slower by at least a factor of 500 than the rate under the optimum preparative conditions described above.

A separate 10-ml. aliquot of the irradiated solution was removed and evaporated to dryness. An infrared spectrum of a carbon tetrachloride solution of the residue gave no indication of the presence of 9,10-dihydrophenanthrene since six major peaks found in the spectrum of an authentic sample of this substance were absent.

The following series of experiments was undertaken in which the conditions described above for the irradiation of stilbene under a nitrogen atmosphere were modified slightly: (a) a mixture of 1.80 g. of trans-stilbene and 19 mg. (1 mole % based on the stilbene) of p-toluenesulfonic acid in 500 ml. of cyclohexane was irradiated for 8 hr.; (b) a mixture of 1.80 g. of trans-stilbene and 190 mg. (10 mole %) of p-toluenesulfonic acid in 500 ml. of refluxing benzene was irradiated for 22 hr.; (c) a mixture of 0.90 g. of trans-stilbene and 95 mg. (10 mole %) of p-toluenesulfonic acid in 250 ml. of 95% ethanol was irradiated for 16 hr.; and (d) a solution of 1.00 g. of trans-stilbene in 400 ml. of acetic acid and 100 ml. of water was irradiated for 15 hr. In no case was any photoisomerization to 9,10-dihydrophenanthrene detected by infrared spectral analysis.

(70) The cis-stilbene was removed in this way since its presence would have complicated the infrared spectral analysis for phenanthrene.