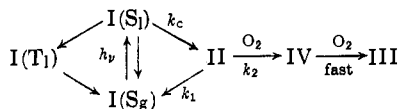lowed kinetically by absorbance measurements at 312.8 mμ.

The presumed mechanism is outlined below.

The precursor of II is believed[1] to be I in the first excited singlet state, S_1,[2] which either cyclizes to II or gives back I in the ground singlet state, S_g, by various paths, one of which could involve the triplet-state molecule $I(T_1)$. The intermediate II is expected[1] to undergo thermal ring opening to give $I(S_g)$ or to undergo hydrogen abstraction by oxygen to give a radical (IV) which very rapidly undergoes a second abstraction to give III. The rate expression is $d[III]/dt = (1/V)\phi I_{abs_1}$ where V is the volume of the reacting solution, ϕ is the quantum yield of III, and I_{abs_1} is the intensity of light absorbed by I. Now ϕ can be expressed as $q \times f$ where q is the quantum yield of II and f is the fraction of the II produced which reacts to give III. The expression for f is $k_2[O_2]/(k_1 + k_2[O_2])$ where k_2 is the bimolecular rate constant for the first hydrogen abstraction from II and k_1 is the unimolecular rate constant for the ring opening of II. From the kinetic measurements and knowledge of the incident light intensity on the cell and the absorptivities of I and III values of ϕ were obtained.

The value of ϕ measured in an oxygen-saturated solution exceeded that measured in an air-saturated solution for each of the four triphenylethylenes by the same factor, $\phi_{O_2}/\phi_{air} = 1.27 \pm 0.01$. That is, the relative quantum yields, ϕ_X/ϕ_H, were independent of $[O_2]$ in the range investigated. It can be shown that the only reasonable conclusion to be drawn from these results is that q is independent of $[O_2]$ and f is independent of the substituent X. It is plausible that q should not depend on $[O_2]$ since $I(S_1)$ is probably extremely short-lived by analogy with the stilbenes.[3] The lack of dependence of f on X can be rationalized easily. The ring opening of II is estimated[1] to be exothermic by about 35 kcal./mole; this exothermicity implies that the transition state for this process resembles II with the carbons at which bond breaking is occurring being essentially tetrahedral and saturated. In such a system the substituent X is too remote to be expected to exert an appreciable influence. Furthermore, hydrogen abstraction from II is believed to give IVa rather than IVb since in IVa the radical would be stabilized by the phenyl group but not, to a first approximation, by the substituent X, whereas in IVb the situation would be reversed. The assumption that the
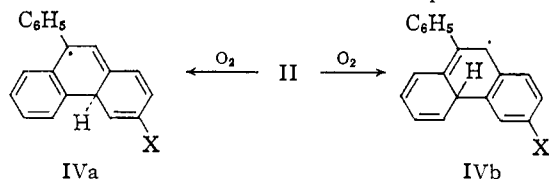
concentration of dissolved oxygen in the oxygen-saturated solutions was five times that in the air-saturated solutions gave $f_{O_2} = 0.93$ and $f_{air} = 0.73$, and thus allowed the evaluation of the q's ($q_{CH_3} = 0.071$, $q_H = 0.059$, $q_{CH_3O} = 0.046$, $q_{Cl} = 0.023$).

It is of interest to determine whether the effects of substituents on the reaction rates of molecules in electronic excited states are similar to those known from studies of molecules in electronic ground states. In general, an electronically excited molecule which undergoes some chemical reaction (such as isomerization, dissociation, or a bimolecular reaction) with a rate constant[4] k_c in sec.$^{-1}$ will also undergo competitive loss of excitation energy (by emission of light or by various radiationless processes) with an apparent rate constant k_d in sec.$^{-1}$, where k_d is the sum of the individual rate constants[4] for all the deactivating processes. These rate constants are related to the quantum yield for the reaction, q, by the expression $k_c/k_d = q/(1 - q)$; the ratio of the k_c's for two members of a series of related compounds differing only in the identity of one substituent would be given (except for cases with $q = 1$) by the product of three factors

$$\frac{k_{c_1}}{k_{c_2}} = \left(\frac{q_1}{q_2}\right)\left(\frac{1 - q_2}{1 - q_1}\right)\left(\frac{k_{d_1}}{k_{d_2}}\right)$$

Thus, it is not possible to use relative quantum yields, q_1/q_2, as measures of relative rate constants, k_{c_1}/k_{c_2}.[5]

We have tentatively assumed that k_d is independent of X for the four triphenylethylenes studied. The justification for this assumption will be argued later. A Hammett plot of log $[q_X(1 - q_H)/q_H(1 - q_X)]$against the σ_m constants for the substituents X gave a straight line (correlation coefficient 0.9996) with slope -1.15. This result is interpreted to indicate the existence of activation energy barriers to the $I(S_1) \rightarrow II$ reactions whose magnitudes depend on X. This reaction is calculated[1] to be exothermic by about 50 kcal./mole so the transition state should closely resemble the reactant, $I(S_1)$; it is reasonable, therefore, that the substituent X should transmit its effect to the reaction site in the fashion for which σ_m parameters are applicable. The negative slope of the Hammett plot is thought to arise from the necessity for electron withdrawal from the pi system to form the new C–C sigma bond. Preliminary measurements have shown that the temperature dependence of the rates is extremely small (E_a's ca. 1 kcal./mole) with the slowest compound (I with X = Cl) having the largest dependence, in further accord with the interpretation given above.

(4) For bimolecular processes the k's would be pseudo unimolecular rate constants.

(5) H. Ziffer and N. E. Sharpless. J. Org. Chem., 27, 1944 (1962).

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THE PHOTOCHEMICAL CONVERSION OF STILBENE TO
PHENANTHRENE. THE NATURE OF THE
INTERMEDIATE

Sir:

The photocatalyzed trans–cis isomerization of stilbene is well known and has been studied in detail.[1] Lewis[2] reported that a slight yellow color was imparted to stilbene solutions during irradiation and that some stilbene was lost in a side reaction. It was later shown[3] that the side reaction produced phenanthrene and this reaction has been further investigated by other groups.[4-6] Schaffner proposed[4] that photolysis of dilute solutions of either trans-stilbene (I) or cis-stilbene (II) produced a common excited state (III) which would convert to excited state IV. Excited state IV would then cyclize, giving intermediate V which would be oxidized in a dark reaction, chiefly by oxygen, to form

(1) See, for example, R. H. Dyck and D. S. McClure, J. Chem. Phys., 36, 2326 (1962), and references cited therein.

(2) G. N. Lewis, T. T. Magel and D. Lipkin, J. Am. Chem. Soc., 62, 2973 (1940).

(3) R. E. Buckles, ibid., 77, 1040 (1955).

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

(5) V. H. Stegemeyer, Z. Naturforsch., 17, 153 (1962).

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

(2) It is also possible that the cyclization is a reaction of $I(S_g)$ in a high vibrational level formed by internal conversion from $I(S_1)$.

(3) H. Stegemeyer, Z. Naturforsch., 17b, 153 (1962); R. H. Dyck and D. S. McClure, J. Chem. Phys., 36, 2326 (1962).

phenanthrene (VI). In support of this mechanism, it was found that 0.92 mole of oxygen was consumed per mole of phenanthrene formed.[7] Phenanthrene
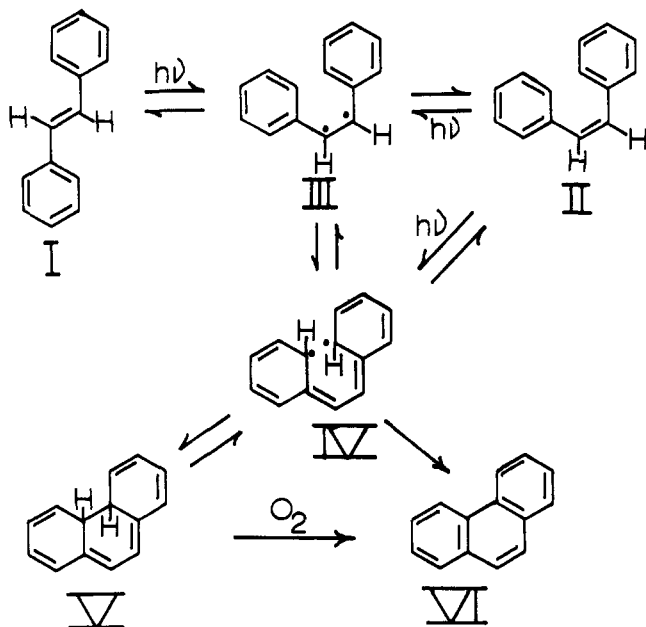
formed very slowly and in poor yield when nitrogen was bubbled through the reaction mixture during photolysis. Stegemeyer,[5] on the basis of quantum yield measurements, proposed that the cyclization proceeds from some excited state (such as IV) which is available only to cis-stilbene and that the trans compound can hence be converted to phenanthrene only through cis-stilbene. It was further proposed[5] that since no previous workers had found evidence for intermediate V and since it was in any case an energetically unlikely structure, the process was a concerted one in which the excited state IV cyclized and lost hydrogen directly to form phenanthrene. Oxygen played no specific role in the conversion. Mallory[6] took an intermediate view, agreeing with the general mechanism of Schaffner, but assuming V would not be isolable at room temperature.

Some preliminary results from our laboratories, in support of Schaffner and contrary to Stegemeyer, provide direct evidence for the existence of intermediate V. Since we have confirmatory evidence of Stegemeyer's proposal that the cyclization proceeds only from cis-stilbene, we believe the reaction path is I–II–IV–V–VI (where IV is an excited singlet state different from that involved in the trans to cis isomerization).

The evidence obtained is: 1. Irradiation[9] of a 5×10^{-3} M solution of trans-stilbene in cyclohexane for two minutes produced a yellow color which disappeared rapidly upon removal of the cell from the reactor. The exposed solution gave a positive test for hydrogen peroxide[11] and an ultraviolet spectrum showed the presence of phenanthrene. An identical solution of trans-stilbene was degassed[12] and photolyzed in vacuo to again produce a yellow solution. The color faded over a period of 2–3 hr. If the cell was

(7) In the similar photoconversion of helianthrone and $\Delta^{10,11}$-dianthrone to meso-naphthodianthrone,[8] a 0.8 to 1.0 mole oxygen uptake per mole of product formed was also observed.

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

(9) Filtered light of wave lengths less than 310 mμ from a photochemical reactor[10] was used. The intensity of the collimated light beam was approximately 10^{16} quanta-sec.$^{-1}$ cm.$^{-2}$, an intensity considerably higher than was used by previous workers.

(10) W. M. Moore and M. Ketchum, J. Am. Chem. Soc., **84**, 1368 (1962).

(11) In the study of Brockmann[8] essentially one mole of H_2O_2 was found per mole of photoproduct formed.

(12) The air was removed by eight or more freeze–thaw cycles under a reduced pressure of 10^{-4} mm.

opened after the color had faded, the spectrophotometric analysis and gas chromatography showed the presence of cis-stilbene and a small amount of trans-stilbene. If the evacuated cell was opened to air immediately after photolysis, phenanthrene was formed.

2. Spectrophotometric analysis of the yellow solution showed that the color was due to an absorption peak at 447 mμ. Kinetic spectrophotometric observation of the exposed solution showed that the 447 mμ peak disappeared in the same time interval as the 252 mμ phenanthrene peak appeared. Irradiation of 5×10^{-4} M, 1×10^{-3} M and 5×10^{-3} M solutions of trans-stilbene gave maximum absorbance at 447 mμ of 0.2, 0.5, 1.5, respectively.

3. Photolysis of a 5×10^{-5} M solution of trans-stilbene with filtered light of 290–310 mμ produced only a trace of phenanthrene as compared with the normal photolysis[13] using all wave lengths below 310 mμ. However, a mixture of stilbenes which was predominantly cis-stilbene was obtained from the reaction. Since cis-stilbene absorbs only slightly in the region 290–310 mμ, the inhibition of phenanthrene formation must indicate that a photo-excited state of cis-stilbene is a precursor of phenanthrene. This result is in agreement with the quantum yield data of Stegemeyer.[5]

4. Photolysis of identical 5×10^{-4} M solutions of trans-stilbene in pentane in vacuo at $-70°$ and at room temperature gave maximum absorbances at 447 mμ of 0.5 and 0.2, respectively. Not only was the concentration higher at the low temperature, but the maximum absorbance was obtained within five minutes as compared to twenty minutes for photolysis of a solution at room temperature. A comparison of these results shows that the intermediate formed nine times faster in the cold solution than at room temperature. Warming of the cold solution to room temperature lowered the absorbance to 0.2. If the solution originally at room temperature was cooled to $-70°$, additional irradiation gave a maximum absorbance of 0.45. These results indicate that an equilibrium exists between stilbene and the intermediate during irradiation. This equilibrium can be shifted in favor of the intermediate by lowering the temperature. The primary process of converting cis-stilbene to intermediate must therefore be more efficient than ordinary rate data would indicate.

We believe the above data provide strong evidence for the existence of V as a discrete intermediate[4] and that the mechanism must involve an excited state of cis-stilbene which is not available to trans-stilbene directly.[5] To permit coupling, the particular excited state immediately prior to the formation of V must be the singlet IV. Compound V is oxidized to phenanthrene in the presence of a hydrogen acceptor, but reverts by a thermal process to cis-stilbene in the absence of such an acceptor.

The extended conjugated system of V does not seem to have a parallel in the literature. It is difficult to apply standard calculations to check the experimental values for the absorbance maximum without known comparison systems. However, modifications of Woodward's rules, carotenoid rules and calculations based on known straight chain analogs all give values for the maximum ranging from 403 to 475 mμ.

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(13) Photolysis times were adjusted so that each solution absorbed the same number of photons.