

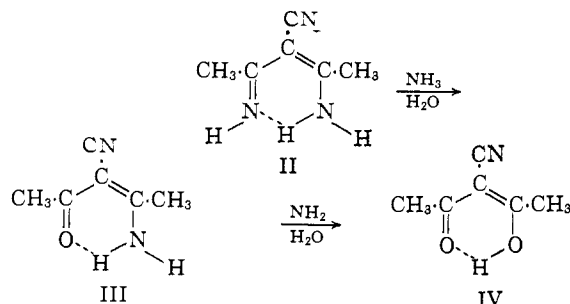
length maximum of I, λ_{\max} 2640 Å. (ϵ_{\max} 3,800) is shifted in II to λ_{\max} 2920 Å. (ϵ_{\max} 11,800), for the neutral forms.

In aqueous medium, at room temperature, II underwent deamination at pH below 4 or above 9 with loss of one nitrogen to give, quantitatively, III, λ_{\max} 2900 Å. (ϵ_{\max} 14,700). The latter, in dilute alkali at room temperature, was further deaminated with loss of one nitrogen to give, quantitatively, IV⁴ which, on crystallization from dilute acid, m.p. 52.5–53.0°, had a molecular weight and elementary analysis corresponding to C₆H₇NO₂ and λ_{\max} 2760 Å. (ϵ_{\max} 10,300) for the neutral form.

Compound IV exhibits an acid function, pK = 3.5, but the infrared spectrum shows neither the carbonyl nor the OH stretching frequencies typical for a normal carboxyl group. There is, instead, a broad, weak, band in the region 2850–2450 cm.⁻¹ (attributable to a strongly bonded OH group, and a strong, broad, band centered at 1598 cm.⁻¹ which may be due to the C=O stretching vibration in either a strongly internally hydrogen-bonded carboxyl group or an enolic β -diketone. There is also a strong, sharp, band at 2220 cm.⁻¹, present also in II and III, but absent in I, indicative of the presence of either a cumulative double bond or a nitrile group. The latter possibility was at first disregarded because of the remarkable stability of IV in acid and alkali. For the same reason the similarity in melting point and elementary composition of IV to the cyanoacetylacetone described by Traube⁵ was initially regarded as coincidental.

Recourse was then had to n.m.r. In carbon tetrachloride IV exhibits a sharp peak at 7.62 (all values in p.p.m., SiMe₄ measured at 40 Mc.) ascribed to methyl groups and a broad peak at -6.80 assigned to OH groups, the low field position for the latter being characteristic for a β -diketone, e.g., for acetylacetone the absorption is at about -6. In addition both the methyl groups of I were found in II and appeared to be equivalent; the presence of two methyl groups in II was further substantiated by an examination of III (see below).

The foregoing findings, together with the infrared evidence, led us to prepare Traube's acetylacetone, the properties of which proved indeed to be identical with those of IV. Furthermore the dissociated form of IV exhibits a bathochromic shift in λ_{\max} to 2800 Å. (ϵ_{\max} 18,000) which finds its counterpart in the dissociated form of II, λ_{\max} 2980 Å. (ϵ_{\max} 22,000). The locations of these maxima and, in particular, their high extinction coefficients, indicate a common skeletal structure differing from I and in line with that for acetylacetone derivatives. The formula of IV, and its formation from II, is therefore as follows



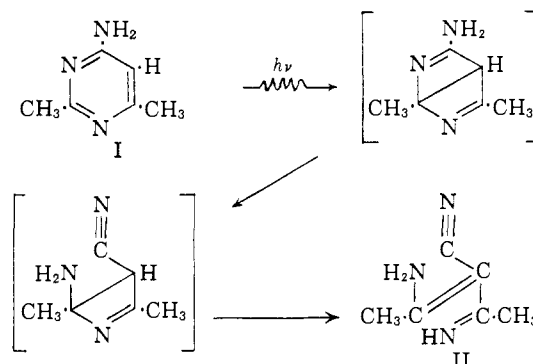
From the foregoing it is clear why the methyl groups in II (2-amino-3-cyanopent-2-ene-4-imine) and IV (3-cyanopent-2-en-2-ol-4-one) appear to be equivalent on time average by n.m.r. In III (2-amino-3-cyano-

(4) Deaminations were carried out at 100° for preparative purposes.

(5) W. Traube, *Ber.*, **31**, 2938 (1898).

pent-2-en-4-one), on the other hand, there is a singlet at 7.66 assigned to CH₃CO; the other methyl peak, at 7.67, is split by the amino protons. Additional ultraviolet, infrared and n.m.r. data are in accord with the above and will be presented in full detail elsewhere. The stability of the nitrile group in II, III and IV toward acid and alkali at elevated temperatures can now be understood in terms of the resonance stabilization resulting from "conjugate chelation."⁶

A tentative mechanism for formation of II from I is



While there is no direct evidence for the unstable Dewar-like intermediates, a radical path not involving bridging would require that the reaction proceed *via* at least two steps. We consider this unlikely in view of the first-order course of the reaction and the formation of only one primary photoproduct (II). This is being investigated further.

The elucidation of this photochemical reaction is expected to be of considerable assistance in clarifying the nature of the photochemical transformations of other 4-aminopyrimidines and, particularly, of the various cytosine analogs^{1,2} which are of current importance in the photochemistry of nucleic acids.

(6) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1068 (1949); J. Weinstein and G. M. Wyman, *J. Org. Chem.*, **23**, 1618 (1958).

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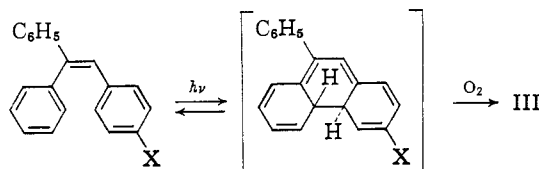
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RECEIVED NOVEMBER 10, 1962

PHOTOCHEMISTRY OF STILBENES. II. SUBSTITUENT EFFECTS ON THE RATES OF PHENANTHRENE FORMATION

Sir:

In further studies¹ of the photochemical conversion of stilbenes to phenanthrenes we have determined the effects of substituents on the rates of conversion of the substituted triphenylethylenes (I) *via* the presumed intermediate dihydrophenanthrenes (II) to the corresponding 3-X-9-phenylphenanthrenes (III) where X = H, CH₃, CH₃O, or Cl.

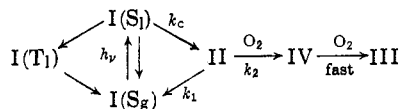


Magnetically stirred cyclohexane solutions, ca. 4×10^{-5} M in triphenylethylene and saturated either with air or with oxygen at 30°, were irradiated in a quartz cell with filtered light of wave lengths 312.5–313.1 m μ from a mercury arc.¹ The reactions were fol-

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

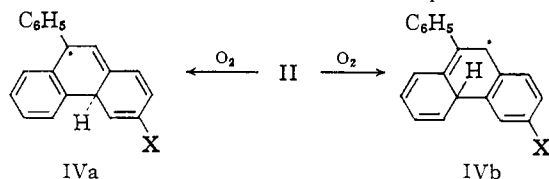
lowed kinetically by absorbance measurements at 312.8 μ .

The presumed mechanism is outlined below.



The precursor of II is believed¹ 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 expected¹ 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 $d[\text{III}]/dt = (1/V)\phi I_{\text{abs}}$ where V is the volume of the reacting solution, ϕ is the quantum yield of III, and I_{abs} 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 $k_2[\text{O}_2]/(k_1 + k_2[\text{O}_2])$ 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, $\phi_{\text{O}_2}/\phi_{\text{air}} = 1.27 \pm 0.01$. That is, the relative quantum yields, ϕ_X/ϕ_H , were independent of $[\text{O}_2]$ 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 $[\text{O}_2]$ and f is independent of the substituent X. It is plausible that q should not depend on $[\text{O}_2]$ 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 estimated¹ 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 $f_{\text{O}_2} = 0.93$ and $f_{\text{air}} = 0.73$, and thus allowed the evaluation of the q 's ($q_{\text{CH}_3} = 0.071$, $q_{\text{H}} = 0.059$, $q_{\text{CH}_3\text{O}} = 0.046$, $q_{\text{Cl}} = 0.023$).

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 under-

(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).

goes some chemical reaction (such as isomerization, dissociation, or a bimolecular reaction) with a rate constant⁴ 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 constants⁴ 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

$$\frac{k_{c1}}{k_{c2}} = \left(\frac{q_1}{q_2}\right) \left(\frac{1 - q_2}{1 - q_1}\right) \left(\frac{k_{d1}}{k_{d2}}\right)$$

Thus, it is not possible to use relative quantum yields, q_1/q_2 , as measures of relative rate constants, k_{c1}/k_{c2} .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 $I(S_1) \rightarrow \text{II}$ reactions whose magnitudes depend on X. This reaction is calculated¹ 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 Lewis² 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 shown³ that the side reaction produced phenanthrene and this reaction has been further investigated by other groups.⁴⁻⁶ Schaffner proposed⁴ 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).