state nature. This explains the correlation of numerous electrophilic aromatic substitutions of the "late transition state" type with σ^+ in the linear free energy relationship[8] (frequently called the "Brown Selectivity Relationship"). This relationship fails, however, when more reactive electrophiles are involved giving increasingly "early transition states" with structures resembling starting materials. For these cases, σ^+ constants are obviously not suited, because they are derived from benzylic systems reflecting primarily conjugative effects and not ground-state inductive effects.

The realization that the extent of resonance and inductive interaction in the transition state depends on the electron demand of the reagent has indeed led to the view that satisfactory correlation of electrophilic substitutions requires the introduction of more than one parameter which measures the importance of these interactions. The most successful treatment of this type so far is that of Yukawa and Tsuno[9] and it indeed correlates the widely varying erratic electrophilic substitution reactions much better than the Hammett–Brown treatment.

In conclusion, our work proves for the first time in a well-defined electrophilic aromatic substitution reaction where all parameters are kept constant and only the electrophilicity of the reagent is changed systematically through substituents in the reagent itself that the position and thus the nature of the transition state is not a fixed one and can be changed with ease from a late one resembling intermediate (σ complex) to an early one resembling starting material (π complex). The general implications of this concept for the mechanism of electrophilic aromatic substitution will be further emphasized in subsequent publications, including reports of similar effects in other electrophilic reactions of aromatics (acylations, sulfonylations, etc.)

Acknowledgment. Partial support of the work by the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

(8) For a summary see L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(9) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 971 (1959).

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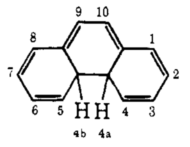
Photocyclization of α,α'-Diethyl-4,4′-stilbenediol. Isolation of a Stable Tautomer of the Elusive Dihydrophenanthrenes

Sir:

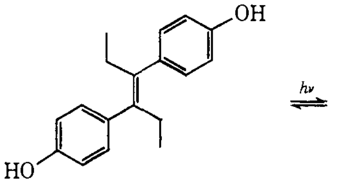
The photochemical oxidative cyclization of stilbenes to phenanthrenes has been the subject of numerous mechanistic studies and has found wide applicability in the synthesis of aromatic and heteroaromatic compounds.[1] Most workers accept a reaction mechanism in which *cis*-stilbene is converted to 4a,4b-dihydrophenanthrene (DHP, **1**) prior to dehydrogenation.



1

Stermitz, *et al.*,[2] presented evidence that the transient visible absorption observed during photolysis of stilbene was caused by intermediate **1**. However, the DHP was not isolated, not only because of oxidation to phenanthrene,[2] but also because of reverse reaction to stilbene.[3] A recent attempt to prepare stable DHP's from styrylnaphthalenes was unsuccessful.[4]

In view of the continuing interest in the intermediate dihydrophenanthrenes, we were prompted to reinvestigate the work of one of us[5] concerning the isolation of stable, crystalline 3,4,4a,4b,5,6-hexahydro-3,6-dioxo-9,10-diethylphenanthrene (**5**) from the irradiation of synthetic estrogenic hormone diethylstilbestrol (*trans*-α,α'-diethyl-4,4′-stilbenediol) (**2**). We now (1) present complete analytical evidence for structure **5**, (2) reformulate the mechanism in terms of a stilbene photocyclization in which intermediate DHP **4** is stabilized by keto–enol tautomerism to the isolable diketone **5**, (3) emphasize that the aromatic hydrogens of **2** which become 4a and 4b in **5** remain intact, *i.e.*, attached to the same carbon atoms,[6] and (4) present indirect evidence that these hydrogens are in a trans configuration.



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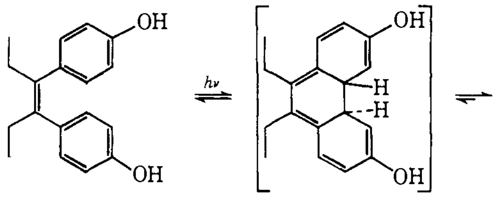
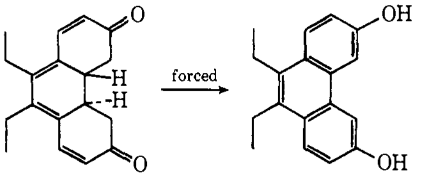


3 **4**



5 **6**

Diketone **5** was prepared by irradiating diethylstilbestrol in aqueous methanol at 254 mμ. Chloroform extraction and recrystallization from toluene–heptane afforded golden-yellow crystals of **5**, which

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(1) For recent reviews see (a) F. R. Stermitz in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 247; (b) E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, **23**, 482 (1969).

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

(3) K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).

(4) E. V. Blackburn, C. E. Loader, and C. J. Timmons, *ibid.*, *C*, 163 (1970).

(5) D. Banes, *J. Ass. Offic. Agr. Chem.*, **44**, 323 (1961).

(6) Rearranged 9,10-dihydrophenanthrene isomers have been isolated: M. V. Sargent and C. J. Timmons, *J. Amer. Chem. Soc.*, **85**, 2186 (1963).

appear to be stable indefinitely. When the solution was buffered with K_2HPO_4, oxidation to 9,10-diethyl-3,6-phenanthrenediol (**6**) was negligible, even in samples open to the atmosphere. However, **6** was the only product obtained from photolyses carried out in acidic media.[7,8]

Elemental analysis of the yellow crystals was consistent with formula **5**. The ir spectrum indicated absence of hydroxyl and presence of highly conjugated carbonyl (1651 cm^{-1}). The electronic absorption in methanol showed λ_{max}, mμ (ϵ, l./mol cm) at 406 (19,600), 287 (23,600), and 221 (8900). The extended unsaturated diketone system of **5** seems without close analogy in the literature; however, adaptation of Woodward's rules[9] predicts absorption in the 400–450-mμ range, as observed.

In addition to characteristic ethyl groups (10 H), the nmr spectrum of **5** showed a doublet pair (4 H) at 6.1 and 7.6 ppm, assigned to the vinyl protons, and a complex multiplet (6 H) in the 2–3-ppm region, partially obscured by the methylene quartet of the ethyl groups. The mass spectrum obtained by direct inlet at 195° gave a base peak at the parent *m/e* 268, as well as prominent peaks at *m/e* 239, 211, 183, and 115 attributable to successive losses of ethyl, ethene, and two carbon monoxide fragments, respectively.

Exchange of the active protons α to the carbonyl groups for deuterium was readily achieved by stirring **5** in $NaOCH_3$-CH_3OD at room temperature for 3 hr. The deuterated product exhibited a mass spectrum similar to that of **5** except that most major peaks were shifted higher by 4 *m/e* units. In addition, loss of 42 *m/e* units (ketene) from fragments of **5** was replaced by a corresponding decrease of 44 *m/e* units in the spectrum of **5**-d_4.[10] The 6 H multiplet at 2–3 ppm in the nmr spectrum of **5** became a 2 H singlet at 2.3 ppm in the spectrum of **5**-d_4, as expected for the now unsplit signal of the 4a and 4b protons. New bands were observed in the ir spectrum at 2211 and 2131 cm^{-1} (C–D stretch).

These results are all in excellent agreement with structure **5**.

Changes in the uv-visible absorption spectrum of dilute (3×10^{-5} *M*) solutions of diethylstilbestrol upon successive short irradiations at 254 mμ indicated efficient and virtually quantitative[11] conversion to **5**. The presence of an isosbestic point at 267 mμ in these consecutive-spectra diagrams testified to the constant molar relationship between product and reactant and to the absence of either dark or photochemical side reactions. The thermal stability of **5**, both toward oxidation to **6** and reversion to **2**, was shown by the absence of change in the electronic spectra of photolyzed solutions stored in the dark for several months. On the other hand, irradiation of **5** in the visible (~400 mμ) or near-uv (366 mμ) caused partial return to **2** or **3**.

As with other stilbenes, the **3** → **5** photocyclization did not proceed in the presence of sensitizers with lowest triplet in proper energetic relationship with that of **3**. Therefore the assignment of either excited singlet[12] or hot ground level[13] as the reacting state seems to hold for stilbene **3** as well.

On the basis of bond energies, the stabilization of diketone **5** relative to its enolic tautomer **4** is estimated to be 37 kcal/mol. When one compares this value with the 39 kcal/mol calculated by Mallory[12] for the expected difference in stability between *trans*-stilbene and unsubstituted DHP, one easily understands why keto-form DHP **5** is isolable, whereas all other reported attempts to isolate a DHP have been fruitless.

There has been uncertainty concerning the geometry of the 4a and 4b hydrogens. Assuming a concerted reaction in a first excited state, the Woodward–Hoffmann orbital symmetry rules[14] predict a conrotatory cyclization with consequent trans configuration for the 4a and 4b hydrogens of **4** and **5**. Steric restraints in the formation of substituted dihydrophenanthrenes also favor trans geometry.[3,15] However, reaction from a hot ground state suggested by quantum mechanical calculations[13] would result in cis configuration. Since *cis*-DHP would undergo facile exothermic elimination of molecular hydrogen,[12] the fact that the mass spectrum of **5** showed only a minor peak (1.3% of M^+) at $M^+ - 2$ provides strong experimental support for the trans configuration.

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(7) Isolation of phenol **6** without detection of **5** on photolysis of **2** in acetic acid was reported previously by P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960).

(8) Phenanthrene **6** has also been synthesized by an alternative route: D. J. Collins and J. J. Hobbs, *Aust. J. Chem.*, **20**, 1905 (1967). A sample kindly sent us by D. J. C. was identical with our material.

(9) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 15.

(10) This is a well-known fragmentation: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 155.

(11) In fact, production of **5** is the basis of a quantitative assay procedure for drug **2**: (a) D. Banes, *J. Ass. Offic. Agr. Chem.*, **43**, 248 (1960); (b) United States Pharmacopeia, 16th rev, Mack Publishing Co., Easton, Pa., 1960, p 217; 18th rev, 1970, p 187.

(12) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

(13) H. Guesten and L. Klasnic, *Tetrahedron*, **24**, 5499 (1968).

(14) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(15) C. E. Ramey and V. Boekelheide, *ibid.*, **92**, 3681 (1970).

(16) From work done in partial fulfillment of requirements for the Ph.D. degree at The George Washington University.

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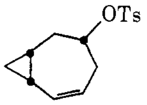
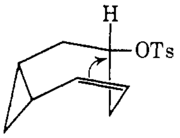
Competitive Homoconjugation between Conformationally Related Species

Sir:

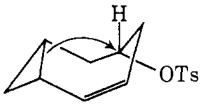
cis-Bicyclo[5.1.0]oct-5-en-3-yl tosylate (*cis*-I-OTs) offers structural features for internal competition between



cis-I



II



III

two types of homoconjugation. The molecule can exist in two conformations (II and III). In II, the double bond is best oriented for participation; in III, the cyclopropane ring. Although II and III may interconvert, the ions they produce, as will be seen, do not.