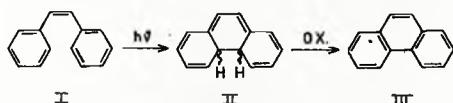


Photodehydrocyclizations of Stilbene-Like Compounds. VI.¹ Chemical Evidence of an Excited State Mechanism

Sir:

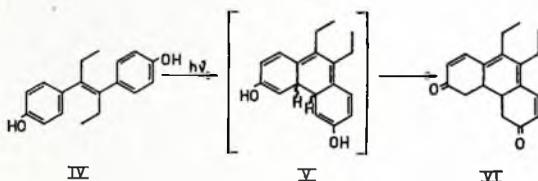
Although the photocyclization of stilbene or analogs into phenanthrene, its derivatives, or benzologs is one of the most studied reactions in organic photochemistry,² Blackburn and Timmons stated in 1969 that the mechanism of the reaction is still the subject of much controversy.^{2b}

The controversy concerns two questions. (a) Is the reactive state an excited singlet state or a vibrationally excited ground state?³ (b) Has the accepted intermediate II a *cis* or a *trans* configuration? The questions are related because orbital symmetry rules prescribe that cyclization in the excited state proceeds conrotatory giving *trans*-II, whereas a ground-state reaction should involve *cis*-II as an intermediate.



Arguments for an excited state mechanism, given by Muszkat and Fischer,³ have been based on fluorescence measurements and quantum yields. Indications for a *trans* configuration of II, based on calculations using Hess' law,⁴ or an extended Hückel MO treatment,⁵ and on the observation that no molecular hydrogen is formed in solution,^{6,7} are consistent with an excited state reaction. However, Güsten and Klasinc⁸ favored a hot ground-state reaction because of the linear correlation between quantum yields of photocyclizations with meta substituted stilbenes and calculated electron densities on the ortho carbon atoms in the ground state.

The major difficulty in the establishment of the mechanism originates in the failure to isolate II and so to elucidate its configuration. Recently, Doyle, *et al.*, isolated,⁹ however, as the irradiation product of α,α' -diethyl-4,4'-stilbenediol (IV) a stable tautomer VI of the primary cyclization product V. We have found that VI reacts as a normal dehydrophenanthrene derivative; on irradiation of a methanolic solution in the presence of iodine at 360 $m\mu$ (outside the absorption range of IV) 9,10-diethyl-3,6-phenanthrenediol was formed in good yield.



(1) Part V: W. H. Laarhoven and Th. J. H. M. Cuppen, *J. Chem. Soc., Perkin Trans. 1*, in press.

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

(3) Sensitization experiments indicate that a triplet state is improbable: K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).

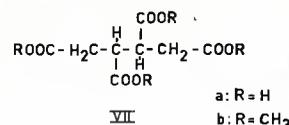
(4) F. B. Mallory, C. S. Wood, and J. F. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

(5) K. A. Muszkat and W. Schmidt, *Helv. Chim. Acta*, **54**, 1195 (1971).

Because IV can be formed back by irradiation of VI, configurations of V and VI must be equal. Doyle, *et al.*, accepted a *trans* configuration because the $M^+ - 2$ peak in the mass spectrum was only a minor peak (1.3%).

Such conclusions from mass spectra should be taken carefully because comparison with *cis* and *trans* isomers of this kind of compounds is not possible.

We found a chemical proof of the *trans* configuration of VI. The compound (500 mg) was ozonolyzed in 50 ml of 80% acetic acid at room temperature for 5 hr. After addition of 20 ml of perhydrol the mixture was boiled for 1 hr, the solvent evaporated *in vacuo*, and the residue taken up in 10 ml of acetone. Dilution with benzene (50 ml) and boiling to remove the acetone yielded 230 mg (54%) of a crystalline product: mp 224–230°; after crystallization from acetone, 234–236° (lit.¹⁰ *rac*-butane-1,2,3,4-tetracarboxylic acid (VIIa), mp 236–237°; *meso*-VIIa, mp 188–189°).



The mixture melting point with authentic *rac*-VIIa¹¹ was undepressed. Esterification of the product with diazomethane gave a tetramethyl ester with mp 61.5–62.5° (lit.¹⁰ *rac*-VIIb, mp 62°; *meso*-VIIb, mp 74–75°). The mixture melting point with authentic *rac*-VIIb was undepressed, with *meso*-VIIb it was 40–55°. Boiling of the product VIIa with acetyl chloride for several hours yielded a dianhydride with mp 172–173° (lit.¹⁰ *racemic*, 172–173°; *meso*, 248°).

The *racemic* configuration of our product could also be established from small differences between the nmr spectra of *rac*- and *meso*-VIIb: *rac*-VIIb δ 3.72 (s, 6 H, 2 CH₃), 3.69 (s, 6 H, 2 CH₃), 3.45–3.26 (m, 2 H), 2.94–2.37 (m, 4 H), $|J_{\text{vio}}| = 4.5$ and 8.5 Hz, $|J_{\text{gem}}| = 16.5$ Hz; *meso*-VIIb δ 3.71 (s, 6 H, 2 CH₃), 3.69 (s, 6 H, 2 CH₃), 3.44–3.23 (m, 2 H), 2.87–2.31 (m, 4 H), $|J_{\text{vio}}| = 4.5$ and 8.5 Hz, $|J_{\text{gem}}| = 16.5$ Hz.

This unambiguous establishment of the *trans* configuration of VI firmly settles in our opinion that photocyclization of IV proceeds in the first excited state.

(6) E. V. Blackburn, C. E. Loader, and C. J. Timmons, *J. Chem. Soc. C*, 163 (1970).

(7) R. Srinivasan and J. C. Powers, *J. Chem. Phys.*, **39**, 580 (1963).

(8) H. Güsten and L. Klasinc, *Tetrahedron*, **24**, 5499 (1968).

(9) F. D. Doyle, N. Filipescu, W. R. Benson, and D. Banes, *J. Amer. Chem. Soc.*, **92**, 6371 (1970).

(10) K. Alder and M. Schumacher, *Justus Liebigs Ann. Chem.*, **564**, 96 (1949).

(11) Authentic samples of *rac*- and *meso*-VIIa were obtained as described by Alder,¹⁰ but the oxidation of the intermediate Diels-Alder adduct was carried out with ozone instead of potassium permanganate or nitric acid. The similarity between our products and those of Alder excludes the fact that unexpected rearrangements or isomerizations may occur during ozonolysis.

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