Tetrahedron Letters No. 18, pp 1789 - 1792, 1972. Pergamon Press. Printed in Great Britain.

PHOTOCYCLIZATION OF STILBENE ANALOGS II. THE PHOTOCHEMISTRY OF 1-BENZYLIDENE-1,2,3,4-TETRAHYDROPHENANTHRENE AND 1-(1-NAPHTHYLMETHYLIDENE)-1,2,3,4-TETRAHYDROPHENANTHRENE

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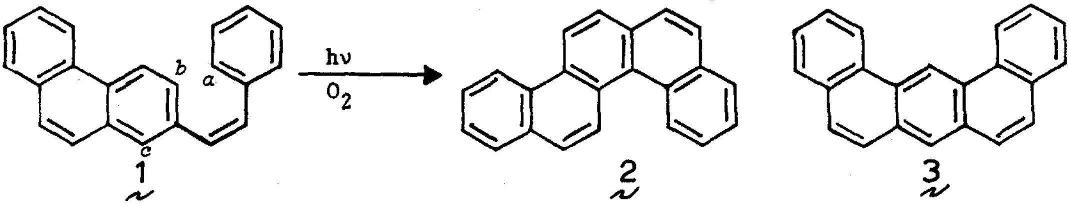
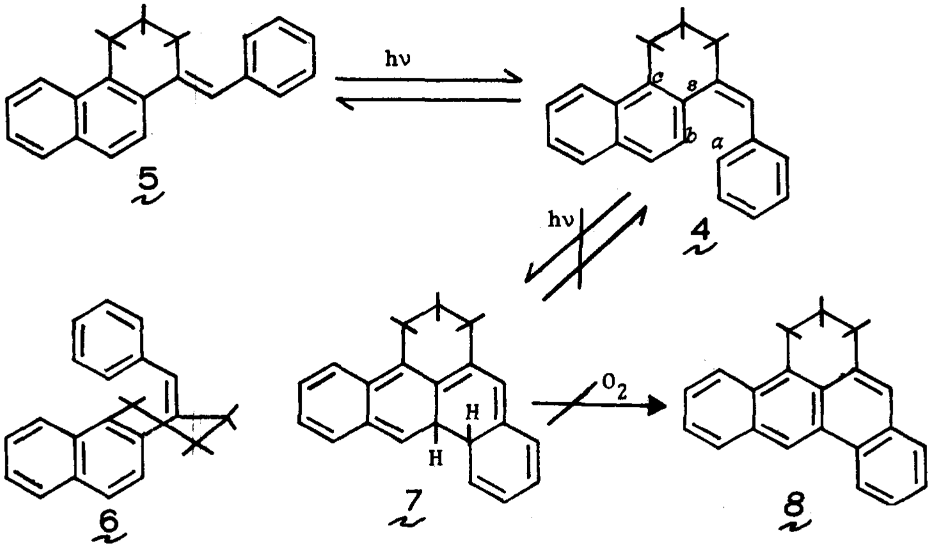
(Received in USA 21 January 1972; received in UK for publication 23 March 1972)

The relative ease of photocyclization of stilbene-like compounds has been related to various quantities derived from HMO theory. Among these, one of the most simple and useful appears to be the sum of the free valence indices in the first excited state, ΣF^*, at the two positions which become bonded during the cyclization (1,2,3). It has been proposed (3) that the higher ΣF^* the greater the ease of cyclization and that if the ΣF^* for two positions is less than 1.0, photocyclization involving these positions does not occur. We have recently shown (4) that with *cis*-2-styrylphenanthrene, **1**, photocyclization occurs almost exclusively at position *c* on the phenanthrene nucleus to yield 99% benzo[c]-chrysene, **2**, but that 1% dibenz[a,j]anthracene, **3**, is formed even though the ΣF^* value for positions *a* and *b* is close to the lower limit of 1.0.



$\Sigma F^* = 1.14$ (*a* + *c*) $\Sigma F^* = 0.99$ (*a* + *b*)

We were interested in learning whether ΣF^* values reflect relative rates for cyclization or if indeed there is a minimum value required below which cyclization will not occur. 1-Benzylidene-1,2,3,4-tetrahydrophenanthrene, 4, is particularly interesting in this connection. The ΣF^* value for positions *a* and *b* is 0.95, while ΣF^* for positions *a* and *c* is 1.17. On this basis, cyclization might be expected to occur at position *c*. However rotation about the single bond *s*, 4, to give the conformation, 6, (which is required for cyclization at position *c*) leads to a very highly strained structure, as was verified by attempted model construction. Thus, were cyclization of 4 to occur, it should proceed via position *b* which has ΣF^* of *a* + *b* of 0.95. Such cyclization would lead to compound 7, which although unknown, appears to have a perfectly reasonable structure.



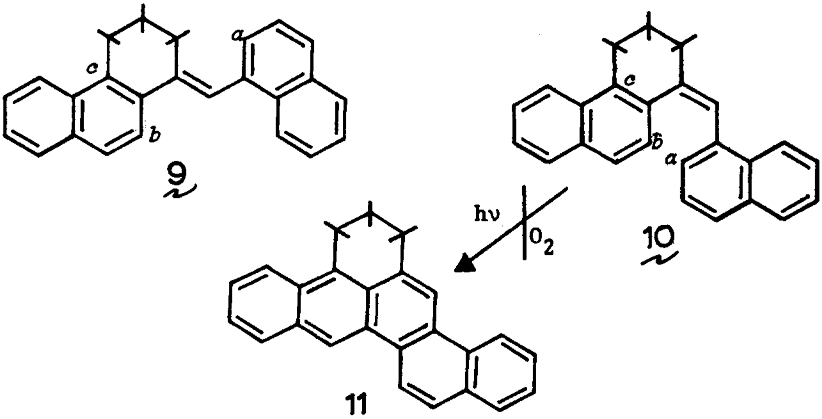
Compound 5, mp 133-135° (5) was obtained from the reaction of 1-oxo-1,2,3,4-tetrahydrophenanthrene (6) with benzylmagnesium chloride followed by dehydration of the intermediate alcohol with a mixture of glacial acetic acid--concentrated HCl (50:1). Pmr spectrum ($CDCl_3$): 1.97δ, quintet, 2H; 2.83δ, triplet, 2H; 3.17δ, triplet, 2H; 7.63δ, multiplet, 12H. Based on the method of preparation, 5, is assigned the *trans* configuration.

A 1 X 10^{-5} M solution of 5, in cyclohexane, was placed in a quartz test tube and irradiated in the presence of adventitious oxygen, with light from a medium pressure 550 watt mercury arc (Hanovia 673A). The irradiation was continued until the absorption spectrum remained constant (0.25 hr). The absorption spectrum did not resemble that expected (7) if 8 were present to any extent. It is reasonable to assume that 8 would be readily formed by oxidative dehydrogenation of 7 in the presence of oxygen. Gas chromatographic analysis (8) of the solution showed two peaks, one (62.8 ± 2%), identical to the *trans* starting material the other (37.2 ± 2%), with a shorter retention time was assumed to be the *cis* isomer, 4.

In a second experiment, a 1 X 10^{-2} M solution of 5, in cyclohexane, was placed in a quartz cell and degassed using five freeze-pump-thaw cycles at 10^{-6} torr. Following irradiation, analysis of the reaction mixture, showed it to be identical to that obtained after irradiation under aerobic conditions.

trans-1-(1-Naphthylmethylidene)-1,2,3,4-tetrahydrophenanthrene, 9, was prepared by the reaction of 1-naphthylmethylmagnesium chloride with 1-oxo-1,2,3,4-tetrahydrophenanthrene followed by dehydration of the alcohol with a glacial acetic--hydrochloric acid mixture, mp 130-132° (5). Pmr spectrum ($CDCl_3$): 1.88δ, quintet, 2H; 2.57δ, triplet, 2H; 3.08δ, triplet, 2H; 7.57δ, multiplet, 14H.

The photochemistry of 9, an analog of 5, was investigated under the same conditions described for 5. Here the ΣF* values are 0.95 and 1.10 for positions *a* plus *b*, and positions *a* plus *c*, respectively. For this system the ratio of the ΣF* values (1.10/0.95 = 1.158) is essentially equal to that found in 2-styrylphenanthrene (1.14/0.99 = 1.152). If ΣF* values are a measure of the relative rate of cyclization then cyclization of 10 should proceed smoothly to 11 since cyclization to position *c* is sterically blocked. The absorption



spectrum of the product from the photoreaction of **9** was the same when either aerobic or degassed samples were employed. The absorption spectrum of the product was completely different from that expected were **11** present (7). Gas chromatographic analysis showed the presence of 20.3 ± 2% *cis* isomer, **10**, and 79.7 ± 2% *trans* isomer, **9** (8).

The results of this investigation show that photochemical isomerization is the only reaction which **4** and **10** undergo (9). The results found for **10**, when compared with those of **1**, indicate that the ΣF* values probably do not reflect the relative rates of photocyclization. There appears to be a definite threshold value for ΣF*, below which photocyclization is not likely to occur.

References

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2. F. Dietz and M. Scholz, *Tetrahedron,* **24**, 6845 (1968).
3. W. H. Laarhoven, Th. J. H. Cuppen and R. J. F. Nivard, *Rec. Trav. Chim,* **87**, 687 (1968).
4. D. D. Morgan, S. W. Horgan and M. Orchin, *Tetrahedron Letters,* 4347 (1970).
5. Elemental analyses were within the accepted limits.
6. R. D. Haworth, *J. Chem. Soc.,* 1125 (1932).
7. The absorption spectra of authentic samples of benz[a]anthracene and benzo[b]chrysene were obtained and used for comparison.
8. Gas chromatographic analyses were performed on a 3 ft X 1/8 in, 2% versimid 900 on 100/120 chromosorb W column at 250°C.
9. The photocyclization of 2-styrylnaphthalene and 1-(1-naphthyl)-2-(2-naphthyl) ethylene, the sterically unblocked analogs of **4** and **10**, proceeds exclusively in the positions predicted by their respective ΣF* values. See reference 1.