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PHOTOCYCLIZATION OF STILBENE ANALOGS I. THE OXIDATIVE PHOTOCYCLIZATION OF 1,3-DISTYRYLBENZENE(1)

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The photocyclization of *trans*,*trans*-1,3-distyrylbenzene,**1**, in the presence of oxygen, could conceivably produce nine compounds: six intermediate photoproducts (*cis*,*trans*-1,3-distyrylbenzene,**2**, *cis*,*cis*-1,3-distyrylbenzene,**3**, *cis*- and *trans*-2-styrylphenanthrene,**4** and **5**, *cis*- and *trans*-4-styrylphenanthrene,**8** and **9**); and three final photoproducts (benzo[c]chrysene,**6**, dibenz[a,j]anthracene, **7**, 4-phenylpyrene,**10**). Dietz and Scholz (2) reported **6** as the only product from the irradiation of **1** in benzene; they did not isolate any **7** and apparently did not consider the possibility of forming **10**. No experimental verification was reported as to whether 2- or 4-styrylphenanthrene were precursors of **6**. Morgan and Orchin (3) isolated a small quantity of **7** along with **6** from the irradiation of **1** in benzene but were not able to detect any **10**. Laarhoven, Cuppen and Nivard (6) reported that irradiation of **1** gave mainly **6** but they also reported the presence of a small amount of a compound they identified as **10**. Because 4-styrylphenanthrene is a necessary precursor to **10**, they assumed that the former was present during the course of the reaction. However no **7** was found nor could they detect any styrylphenanthrenes.

In view of the above incomplete reports, and as part of our program on predicting the course of cyclization of stilbene analogs we have carried out a more detailed study of the irradiation of 1,3-distyrylbenzene. The three compounds, **1**, (m.p. 170.5-172°, lit.(6) 171°), **5**, (m.p. 206-207°) and **9**, (m.p. 120-121°) were prepared via the Wittig reaction. The photoproducts 2, 3, and 4 were each identified by the appearance of a new peak at a retention time shorter than that of the corresponding *trans* isomer when the products from irradiated degassed samples of the appropriate *trans* isomer were analyzed by VPC. Approximately ten samples of 1, each 2 X 10^{-3} *M* in benzene, were placed in quartz test tubes (dissolved atmospheric oxygen as the oxidant) and irradiated in a merry-go-round reactor with light from a 550 VA medium pressure mercury arc (Hanovia 673A). The light was filtered with a solution filter transmitting the mercury lines between 260-390 nm (7). One test tube was removed periodically and the contents analyzed on a 3 ft. X 1/8 in. 2% versimid 900 VPC column. A plot of percent composition (8) as a function of irradiation time is shown in figure 1 and our proposed reaction path is shown in figure 2.

Although we were unable to detect 3 in runs with oxygen present, it is probably present because 4 is formed faster than 5. The formation of 4 directly from 2 involves both cyclization and isomerization, and is therefor unlikely for

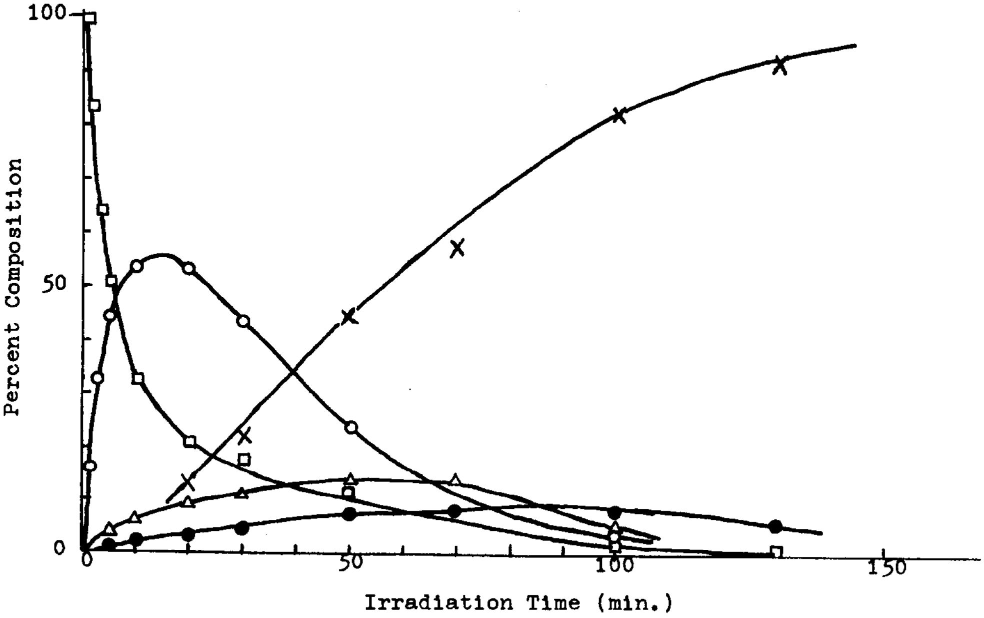

Figure 1. Product distribution from the irradiation of *trans*,-*trans*-1,3-distyrylbenzene; □ -*trans*,*trans*-1,3-distyrylbenzene; ○ -*cis*,*trans*-1,3-distyrylbenzene; ● -*trans*-2-styrylphenanthrene; △ -*cis*-2-styrylphenanthrene; X-benzo c chrysene.

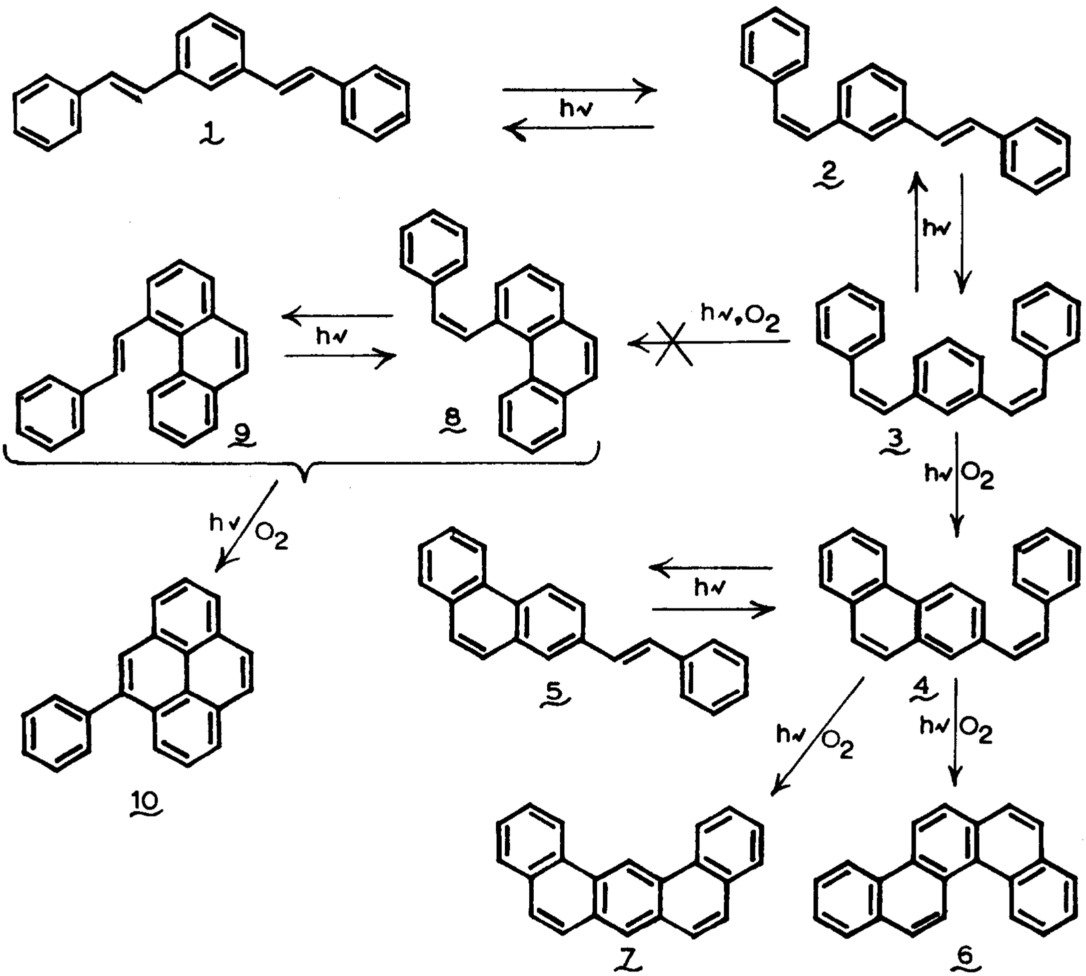

Figure 2. Photoreactions in the 1,3-distyrylbenzene system

a single photon process. Irradiation of a degassed (oxygen free) solution of **1** (five freeze-pump-thaw cycles at 10^{-6} torr), to a photostationary state, gave 52.6 ± 2% **1** and 46.2 ± 2% **2** and ca. 1% of a compound with short retention time which we tentatively identify as **3**. The data suggest that of the distyrylbenzene isomers, only **3** photocyclizes, or that the quantum yield for **2**→**5** is considerably smaller than for **3**→**4**. In the latter stages of the reaction the concentration of **5** exceeds that of **4**. That the photostationary state between **4** and **5** favors **5** was verified by finding 82.8 ± 2% **5** and 17.2 ± 2% **4** after irradiating a degassed sample of **5** to the photostationary state.

The photocyclization of **1** does not proceed through 4-styrylphenanthrene under our reaction conditions since irradiation of **9** in the presence of oxygen gave 72.5 ± 2% **6** and 27.5 ± 2% **10**. If a significant amount of 4-styrylphenanthrene were formed during the irradiation of **1**, **10** would have been observed under our analysis conditions. We are unable to say, at this time, whether **10** arises from **8** or from **9** or from both.

References

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3. (a) D. D. Morgan and M. Orchin, Abstracts, 1st Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 1968, paper 117. (b) Dibenz[a,j]anthracene was isolated from the photolysis mixture by fractional crystallization of the picrate of the crude photoproduct. The red picrate of **7** (m.p. 207-210°, lit.(4) 210°) decomposed in 80% acetic acid to give white crystals of **7** (m.p. 193-196°, lit.(4) 196°) whose UV and phosphorescence spectra were identical to those previously reported (4,5).
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8. The percent composition is based on the assumption that the summation of the percentages of the observed compounds totals 100%. After 200 minutes only **6** (99%) and **7** (1%) are observed.