

PHOTOCYCLIZATION OF SUBSTITUTED 2,2'-DIVINYLBIPHENYL  
DERIVATIVES TO TETRAHYDROPYRENES

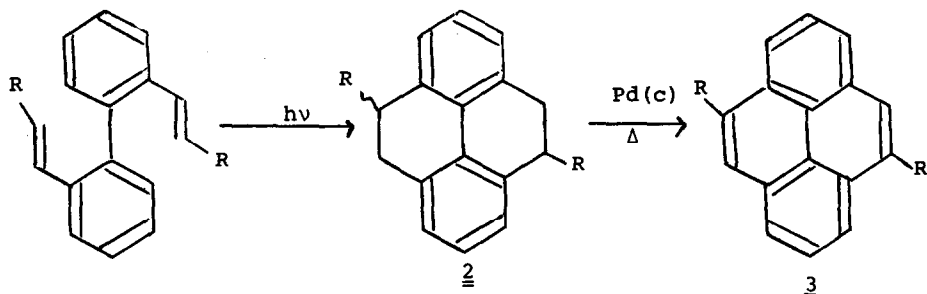
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(Received in USA 14 October 1974; received in UK for publication 8 November 1974)

The photochemical cyclization of stilbene and its derivatives to phenanthrenes has received considerable attention over the past ten years.<sup>1</sup> The mechanism of the photocyclization is generally believed to involve formation of a dihydrophenanthrene derivative and subsequent oxidation of this species. The utility of this reaction as a tool for the synthesis of polycyclic aromatic systems which are difficult to obtain by conventional methods is well established.<sup>1,2</sup> In this communication we wish to report an application of the stilbene-phenanthrene photocyclization reaction which results in the construction of the tetrahydropyrene ring system.

Irradiation of a 0.05M solution of 2,2'-divinylbiphenyl (1a) in benzene with a 450-W Hanovia lamp equipped with a Pyrex filter for 4 hr gave 4,5,9,10-tetrahydropyrene (2a) (80%), mp 134-136°, as the sole photoproduct. The structure of 2a was unambiguously established by comparison with an authentic sample.<sup>3</sup> Similar irradiation of  $\beta,\beta'$ -dicyano-2,2'-divinylbiphenyl<sup>4</sup> (1b) afforded 4,5,9,10-tetrahydro-4,9-dicyanopyrene (2b) (71%), mp 260-262°, as the exclusive photoproduct. When the photolysis of  $\beta,\beta'$ -dicarbomethoxy-2,2'-divinylbiphenyl (1c) was conducted in benzene, a mixture of cis and trans-4,9-dicarbomethoxy-4,5,9,10-tetrahydropyrene (2c), mp 122-129°, was obtained in good yield (60%). Oxidation of the photoproducts to the corresponding 4,9-disubstituted pyrene system (3) could be achieved by heating 2 at 160° in benzene which contained a catalytic quantity of palladium on carbon.



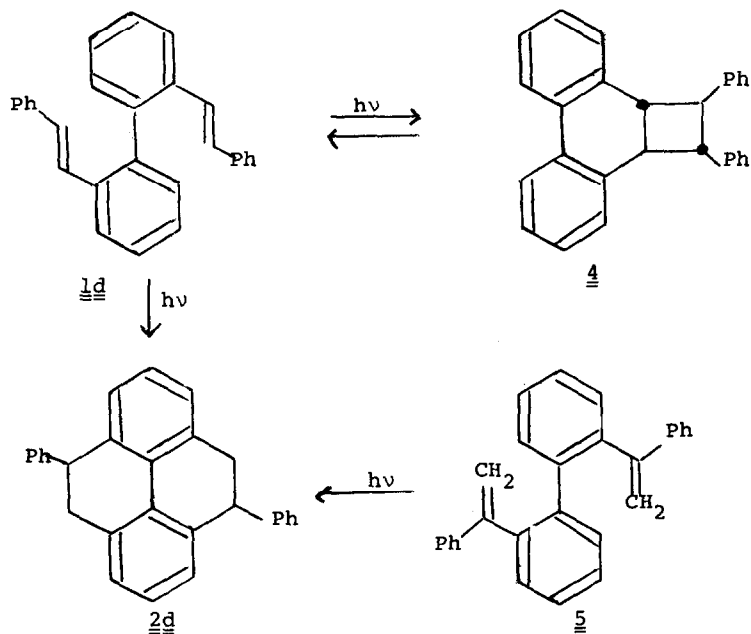
1a; R = H

1b; R = CN

1c; R =  $\text{CO}_2\text{CH}_3$

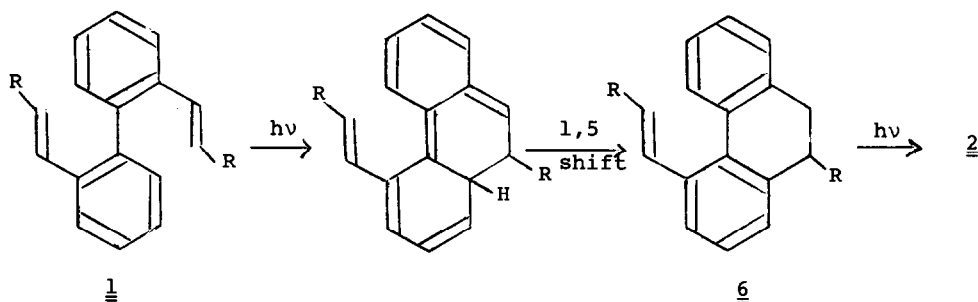
1d; R = Ph

Laarhoven and Cuppen had previously reported<sup>5</sup> that the extended photolysis of 2,2'-distyrylbiphenyl (1d) gave tetrahydro-4,9-diphenylpyrene (2d) as the thermodynamically controlled photoproduct. Irradiation of 1d for shorter periods of time, however, gave 1,2-diphenylcyclobuta[1]phenanthrene (4) as the kinetically controlled product<sup>6</sup> which was ultimately converted into 2d on further irradiation.<sup>5</sup> We have confirmed these findings and have also observed that the irradiation.



ation of  $\alpha,\alpha'$ -diphenyl-2,2'-divinylbiphenyl (5) gave 2d, mp 211-213°, as the exclusive photoproduct even under kinetically controlled conditions. It should be pointed out that the irradiation of all the divinylbiphenyl derivatives studied here (1a-1c) did not lead to any detectable quantities of 2+2 internal cycloadducts, even when short irradiation times were used. This stands in marked contrast to the results of Laarhoven and Cuppen.

The best available evidence indicates that the photocyclization of these 2,2'-divinylbiphenyl derivatives proceeds by a mechanism which involves an initial stilbene-phenanthrene type cyclization followed by a 1,5-sigmatropic hydrogen shift to give a vinyl-substituted phenanthrene (6). On further irradiation, this material is converted to the tetrahydropyrene system. Support for this mechanism was obtained by carrying out the irradiation of 2,2'-divinylbiphenyl (1a) for short periods of time. Under these conditions, a good yield of 4-vinyl-



9,10-dihydrophenanthrene (6a) was obtained. The quantum yield for the cyclization of 1a+6a is 0.074 while that for 6a+2a is 0.026. The quantum yields were not affected when the irradiation was carried out in the presence of piperylene. The photocyclization of 1a to 6a (and 2a) could also be induced by triplet excitation. Thus, irradiation of a solution of 1a through a Uranium glass filter containing sufficient benzophenone to absorb > 95% of the incident light gave 6a as well as 2a. In this case, the quantum yield for cyclization was significant-

ly reduced (ie  $\phi_{\underline{1a} \rightarrow \underline{6a}}$  0.0065 and  $\phi_{\underline{6a} \rightarrow \underline{2a}}$  0.0087). These results would tend to indicate that the singlet state of  $\underline{1a}$  is the reactive state responsible for the cyclization in the direct irradiation experiments.

Acknowledgement: We gratefully acknowledge support of this work by the National Science Foundation (Grant PO-37550). Aid in the purchase of the nmr spectrometer used in this work was provided by the NSF via an equipment grant.

#### References

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