

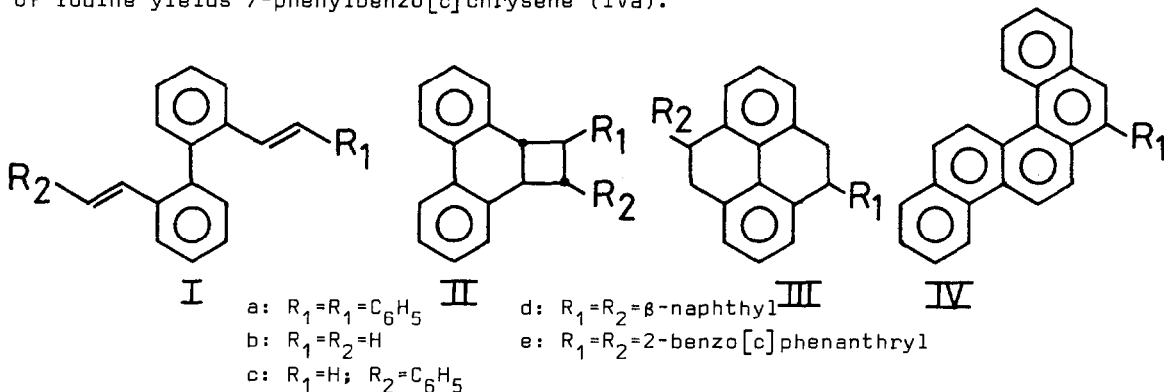
PHOTODEHYDROCYCLIZATIONS OF STILBENE-LIKE COMPOUNDS XIII<sup>1</sup>  
 PHOTOREACTIONS OF  $\alpha$ -SUBSTITUTED 2,2'-DIVINYLBIPHENYLS

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Previously we reported<sup>2</sup> that irradiation of a solution of 2,2'-distyrylbiphenyl (Ia) under anaerobic conditions gives rise to two products: *trans,trans*, *trans*-1,2-diphenyldihydrocyclobutaphenanthrene (IIa) is formed as the kinetically controlled product; whereas 4,5,9,10-tetrahydro-4,9-diphenylpyrene (IIIa) is found to be the thermodynamically controlled compound. Irradiation of Ia in the presence of iodine yields 7-phenylbenzo[c]chrysene (IVa).



Similar reactions with other 2,2'-divinylbiphenyls (Ib-e) revealed now that the nature of the main product not only depends on the experimental conditions but also on the choice of the substituents  $R_1$  and  $R_2$ .

Irradiations of 2,2'-divinylbiphenyl (Ib) (m.p. 81-82<sup>o</sup>) and 2 styryl-2'-vinylbiphenyl (Ic) (m.p. *cis* 54<sup>o</sup>, *trans* 88<sup>o</sup>) in various solvents and at various wavelengths never gave cyclobutane derivatives, neither under nitrogen nor in the presence of iodine. Under anaerobic conditions Ib yielded a mixture of 4,5,9,10-tetrahydropyrene (IIIb, m.p. 134-135<sup>o</sup>C) and a small quantity of its precursor, 9,10-dihydro-4-vinylphenanthrene. Ic gave the corresponding phenyl derivative: 4,5,9,10-tetrahydro-4-phenylpyrene (IIIc) and 9,10-dihydro-9-phenyl-4-vinylphenanthrene. Irradiation of Ib with iodine added as an oxidant caused the same type of ring closure as under anaerobic conditions but the products were 4,5-dihydropyrene and pyrene as a consequence of dehydrogenation steps. However, Ic gave a similar result as Ia under these conditions, benzo[c]chrysene (IVc) being the sole product.

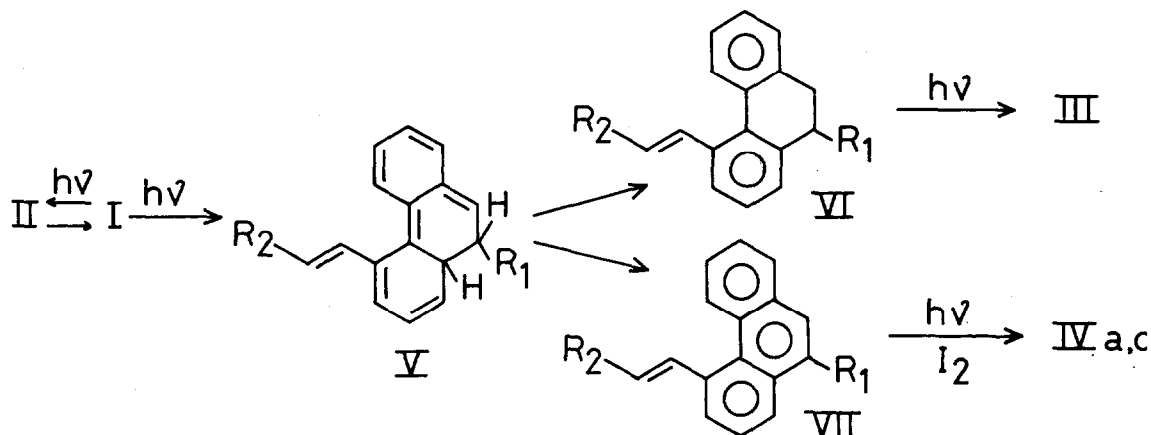
Quite opposite to these results divinylbiphenyls having large aryl residues

at the  $\beta$ -positions (Id, m.p. 141<sup>o</sup>) and Ie (m.p. 234<sup>o</sup>) gave on irradiation under nitrogen as well as with iodine only cyclobutane derivatives (IIId and e), irrespective of the wavelength of the light used (250-360 nm).

Only in one case, Ie irradiated under nitrogen at 300 nm, the presence of a very small amount (<1%) (IIIe) could be deduced in the following way: after oxidation of the reaction mixture with DDQ the characteristic pyrene absorption in the UV spectrum was detected.

Because of the large similarity between the A,A',B,B' pattern of the cyclobutane protons in the NMR spectra of IIId and IIE and that of IIa it could be concluded that the intramolecular cycloaddition in all cases led to a *trans,trans,trans* cyclobutane derivative as had been proven for Ia<sup>1</sup>.

Using the following scheme as a general outline for photochemical reactions of compounds I, it appears that fast intramolecular cycloaddition giving II is only observed if aryl substituents are present at the  $\beta$ -positions of both ethylene groups. This might be due to a preference of these compounds for a conformation in



which the aryl residues are close together<sup>3</sup>. Cyclobutane derivatives from compound I with large aryl residues appear to be quite photostable, possibly because of radiative or thermal loss of excitation energy; with Ia the cycloaddition is apparently reversible. It is not clear if cycloadditions also occur with compounds I having no or only one aryl residue. Anyhow, in these cases the equilibrium I  $\rightleftharpoons$  II should be far to the left, because cyclobutane derivatives could never be isolated. The photoproducts from these compounds arise *via* a common intermediate (V) which undergoes either an irreversible 1,5 hydrogen shift under anaerobic conditions (V  $\rightarrow$  VI) as was demonstrated with 2,3,4,5,6-pentadeutero-2'-styrylbiphenyl, or an irreversible dehydrogenation (V  $\rightarrow$  VII) in the presence of iodine. Under oxidative conditions the latter reaction is much faster than the former with Ia and Ic; Ib gives, however, pyrene (*via* VII) as well as dehydropyrene (*via* VI) on irradiation with iodine.

1. Part XII, W.H. Laarhoven and N.K.J. Kuin, *Rec. Trav. Chim.*, in press.
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3. M.H. de Jongh and W.H. Laarhoven, *Rec. Trav. Chim.*, 92, 673 (1973).