

ORIENTATION IN PHOTOCLEAVAGE OF POLYCHROMOPHORIC CYCLOBUTANES

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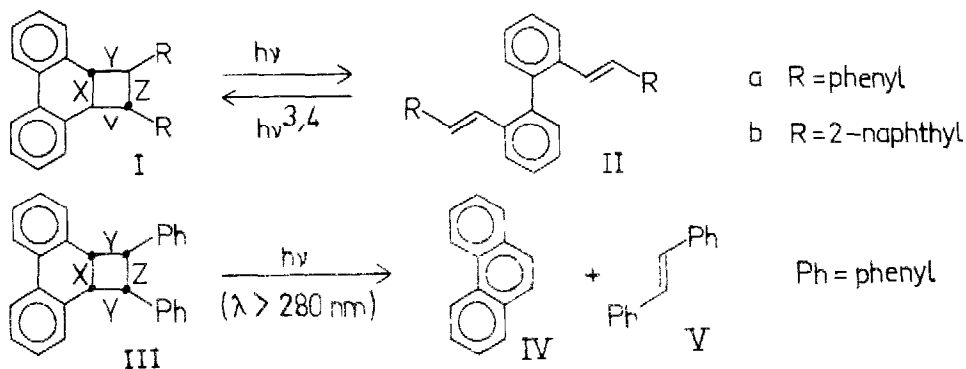
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Orientations in the photocleavage of cyclobutanes<sup>1</sup> are dependent on the arrangement of substituents relative to the light absorbing chromophore. According to a cis-effect<sup>2</sup> those bonds are cleaved preferentially which may release the highest amount of steric interactions. This can be used to rationalize intriguing selectivities irrespective of electronically more or less favourable pathways<sup>2</sup> and may serve to support spectroscopic structure determinations.

The low temperature U.V. spectrum of Ia<sup>3</sup> (-190° in EPA.  $\lambda_{\max}$  = 299, 289, 275, 265, 260 nm) is in accord with a non-planar biphenyl chromophore, whereas the spectrum of III<sup>3</sup> ( $\lambda_{\max}$  = 308.5, 296.5, 288 sh, 283, 278, 271, 268 sh, 263 sh, 255 sh) agrees with a nearly planar system.



Electronic excitation of the biphenyl chromophore in the trans-fused compounds Ia<sup>3</sup> (m.p. 136°) and Ib<sup>4</sup> (m.p. 180-183°) at 300 nm (bandpass 9.6 nm) yields only IIa and IIb. Analysis of the product spectra (IIa.  $\lambda_{\max}$  = 339, 324, 308, 302, 290 sh, 280 sh, 273 sh, 259, 253 sh; IIb 360, 352, 345, 337, 334, 332 sh, 320 sh, 286.5, 275.5, 264.5, 255, 246) on irradiation at -190° demonstrates that they are not contaminated with products of the consecutive reaction at room temperature<sup>3</sup>. Cleavage into IV and V could equally not be detected, whereas 1 % of IV would have been recognized at  $\lambda$  = 292 and 253 nm. On the other hand similar irradiation of cis-fused III (m.p. 177-178°) at 300 nm yields only IV and V<sup>5</sup>.

Clearly as expected from consideration of molecular models<sup>2,3</sup>, cleavages of

