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ORIENTATION IN PHOTOCLEAVAGE OF POLYCHROMOPHORIC CYCLOBUTANES

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Orientations in the photocleavage of cyclobutanes¹ are dependent on the arrangement of substituents relative to the light absorbing chromophore. According to a <u>cis-effect</u>² 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 pathways² and may serve to support spectroscopic structure determinations.

The low temperature U.V. spectrum of Ia³ (-190[°] in EPA.) = 299, 289, 275, 265, 260 nm) is in accord with a non-planar biphenyl chromophore, whereas the spectrum of III³ () = 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 piphenyl chromophore in the trans-fused compounds Ia³ (m p 136°) and Ib⁴ (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 temperature³. 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 <u>cis</u>-fused III (m.p. 177-178°) at 300 nm yields only IV and V⁵.

Clearly as expected from consideration of molecular models^{2,3}, cleavages of

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bond X in I and of bond Y in III are preferred because these offer maximum release of steric strain (in I stretching of bond Y, but not of X, will increase the interaction between ortho and benzylic hydrogens, in III stretching of bond X will create rather than release steric strain).

On excitation of the phenyl groups in Ia and III (at $\lambda = 253.7$ nm) or the naphthyl groups in Ib (at 313 or 253.7 nm) either bond Y or bond Z might be cleaved. I should and does choose cleavage of bond Z for the same reason as pointed out above. Besides II there is found no IV within the limits of error.

In III, however, the electronically excited phenyl groups experience <u>cis</u>-interactions in two directions. This must give rise to cleavages of both bonds Y $(\rightarrow$ IV+V) and Z (\rightarrow IIa). This is found indeed, the product ratio being 4.6/1 at -190°.

 $III \xrightarrow{300 \text{ nm}}_{100\%} IV + V$ $II \xrightarrow{253.7\text{nm}}_{18\%} III \xrightarrow{253.7\text{nm}}_{82\%} IV + V$

The wavelength effect on photolysis of III is a consequence of its polychromophoric nature. The contribution of the phenyl groups to the absorption at 253.7 nm is 35 % (at 25° and -190°) as determined by comparison of the U.V. spectrum and the corrected excitation spectrum for the common⁶ fluorescence of the biphenyl chromophore in III (\emptyset fl = 0.020, λ_{max}^{corr} = 316, 328, 340 sh, 357 sh; cyclohexane). This indicates almostrandom cleavage of bonds Y and Z after electronic excitation of the phenyl groups in III, if it is assumed, that the amount of back reactions from biradical species formed on initial bond cleavage is negligible and as biphenyl excitation leads to very efficient cleavage (\emptyset = 0.75; 308 nm, 25° , CH₂CN).

Further support to these interpretations is provided by the absence of independent fluorescence by the phenyl groups of III in the region of 285 nm 2 (#fl < 5.10⁻⁴). In accordance with the all <u>cis</u>-structure the extreme steric interactions promote chemical deactivation rather than fluorescence. REFERENCES

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