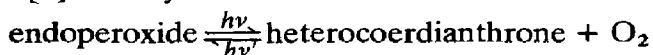


Wavelength-dependent and adiabatic photochemistry of endoperoxides of aromatic hydrocarbons

H.-D. BRAUER, W. DREWS and R. SCHMIDT

Institute for Physical Chemistry, University of Frankfurt am Main, Robert-Mayer Strasse 11, D-6000 Frankfurt am Main 1 (F.R.G.)

In 1969 Kearns and Khan developed a state correlation diagram and predicted a type of photoreaction that had not been observed before in solution: an adiabatic cycloreversion of the endoperoxide into the parent hydrocarbon and oxygen originating from an upper excited singlet state [1]. We were the first to verify this prediction experimentally for the endoperoxide of heterocoerdianthronone [2]. The system



proved to be a highly reversible photochromic system.

In search of further photochromic systems we prepared two other new endoperoxides. The photochemistry of both compounds was again adiabatic and wavelength dependent. The quantum yield of the cycloreversion was constant in the range of the S₂ bands and decreased strongly in the long-wavelength region. During the photochemical cycloreversion, singlet oxygen and hydrocarbons were produced in equal amounts.

1 D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, 10 (1969) 193.

2 R. Schmidt, W. Drews and H.-D. Brauer, *J. Am. Chem. Soc.*, 102 (1980) 2791.

Photophysical study of conformers of naphthylpyridylethylenes

G. G. ALOISI, G. BARTOCCI, F. MASETTI and U. MAZZUCATO

Istituto di Chimica Fisica, Università di Perugia, Via Elce di Sotto 8, I-06100 Perugia (Italy)

The conformational equilibria recently described for several non-rigid stilbene-like molecules were studied for the three isomeric *trans*-1-(2-naphthyl),2-(*n*-pyridyl)ethylenes (*n* = 2,3,4) in fluid solution and in a rigid matrix. Excitation and emission spectra, quantum yields and lifetimes of fluorescence showed the existence of at least two rotational conformers, probably involving the quasi-single bond between the naphthyl group and the ethylenic carbon atom. The relative contributions of the conformers change with temperature and depend on the heteroatom position. The fluorescence analysis allowed us to obtain the photophysical parameters of the two species from those of the mixture and to explain the anomalies observed in the photochemistry of naphthylpyridylethylenes.