The Sensitization of Stilbene Isomerization

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DURING a study of the photochemical characteristics of pyrylium salt dyes, we have discovered what may prove to be a class of sensitizers which do not conform to the theory advanced by G. S. Hammond[1] to correlate photochemical product distributions with sensitizer triplet excitation energies (E_T).

Specifically, we found that the photostationary product ratios in the *cis–trans*-isomerization of stilbene sensitized by several heterocyclic perchlorates did not depend upon E_T in the manner predicted by the theory (Table). The quantum yield for *cis*- to *trans*-isomerization was found to be $0{\cdot}113 \pm 0{\cdot}003$ when 2,4,6-triphenylpyrylium perchlorate was the sensitizer (ferrioxalate actinometer[3]).

TABLE

Product ratios for the cis–trans-*photoisomerization of stilbene sensitised by charged heterocycles*

	E_T (kcal./mole)	Percent *trans*-stilbene at photostationary state	
		Found	Predicted (ref.1)
2-Methyl-4,6-diphenylpyrylium	56	87 ± 9[a]	23
2,4,6-Triphenylpyrylium (I)	53	96 ± 1	14
2,4,6-Triphenylthiapyrylium	52	98 ± 1	10
2,4,6-Tris(4-methoxyphenyl)pyrylium	51	56 ± 0·2	7
2,4,6-Tris(4-methoxyphenyl)-*N*-methyl pyridinium	59	43 ± 1	30

[a] 95% confidence limit of analysis.

Under our reaction conditions, benzil produced a photostationary state containing 93 ± 1% *cis*-stilbene (lit.,[2] 92%), pyrene, 91 ± 2% (lit.,[1] 93%).

The photostationary states were approached from the all-*cis* and from the all-*trans* sides. At least two different exposure times were used in all cases to ensure that the photostationary state was, in fact, independent of time as well as of the starting stilbene isomer. Control experiments were run in several cases to demonstrate that more than 90% of the stilbene could be recovered, that dark isomerization of *cis*- to *trans*-stilbene was negligible (less than 10% at the longest irradiation time), and that the absorption spectrum of the sensitizer was not affected by irradiation.

The heterocyclic cations were synthesized by conventional methods.† They were recrystallized before use and had satisfactory elemental analyses. *cis*-Stilbene was purified by vapour-phase chromatography, followed by distillation, and contained 1—2% of the *trans*-isomer. All other materials were either commercially purified samples or were recrystallized before use.

Acetonitrile solutions comprising stilbene and sensitizer at 5·0 mmole/l. concentration contained in Pyrex glass tubes were deaerated by means of several freeze-evacuate-thaw cycles and sealed. Irradiation was carried out in a "merry-go-round" device similar to that described elsewhere[4] at 25 ± 2°. The light source was a 550w medium-pressure Hanovia mercury arc filtered by Corning glass filters (No. 7380 for photo-stationary-state experiments; No. 7380 and No. 5840 for quantum-yield measurements) to ensure that none of the light was directly absorbed by the stilbenes. Analysis after irradiation was by vapour-phase chromatography on Apiezon L columns. Phosphorescope of conventional design on samples dissolved in solid poly(methyl methacrylate).

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