

## Photolytic Desulphurization of Dibenzoylstilbene Episulphide

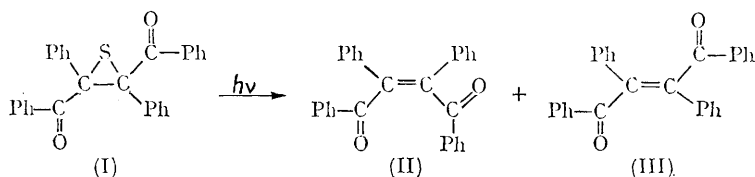
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PAST investigations<sup>1</sup> have established that under appropriate reaction conditions olefins may be formed by the removal of sulphur from episulphides. Reagents which are known to be effective for this are the organolithium compounds,<sup>2</sup> Grignard reagents,<sup>3</sup> and tervalent phosphorus compounds.<sup>4,5</sup> Certain episulphides have also been thermally degraded to an olefin and sulphur.<sup>6</sup> We describe here the photo-extrusion of sulphur

were identified by infrared and ultraviolet spectroscopy and by comparison of their properties with those of authentic samples.

Interestingly, the photodesulphurization is markedly stereospecific. Consideration of the isomeric distribution of the olefin obtained in a number of photolyses and the irradiation time demonstrated at least 90% stereoselective removal of sulphur from (I) to give (III). Increasing the



from dibenzoylstilbene episulphide (I) by ultraviolet light filtered through Pyrex glass.<sup>7</sup>

Irradiation of *trans*-dibenzoylstilbene episulphide<sup>8</sup> (I) with a Pyrex filter in benzene as solvent afforded a mixture of *cis*- and *trans*-dibenzoylstilbene (II and III) in high yield. The photolysis was followed by infrared spectroscopy and was essentially complete in 30–60 min. The products

time of the irradiation gave a slightly higher proportion of the *cis*-olefin but resulted in a diminished overall yield of the olefinic material. The lower yields can be attributed to a competing side reaction which predominates at longer photolysis time.

The loss of sulphur from the episulphide upon photolysis is most simply explained by assuming a

<sup>1</sup> For a recent compilation of references, see the review of D. D. Reynolds and D. L. Fields, "Heterocyclic Compounds with Three and Four Membered Rings", Part I, A. Weissberger, ed., John Wiley and Sons, Inc., New York, N.Y., 1964, p. 576.

<sup>2</sup> N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, 1959, **81**, 578.

<sup>3</sup> F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *J. Amer. Chem. Soc.*, 1954, **76**, 1082.

<sup>4</sup> M. J. Boskin and D. B. Denney, *Chem. and Ind.*, 1959, 330.

<sup>5</sup> R. E. Davis, *J. Org. Chem.*, 1958, **23**, 1767.

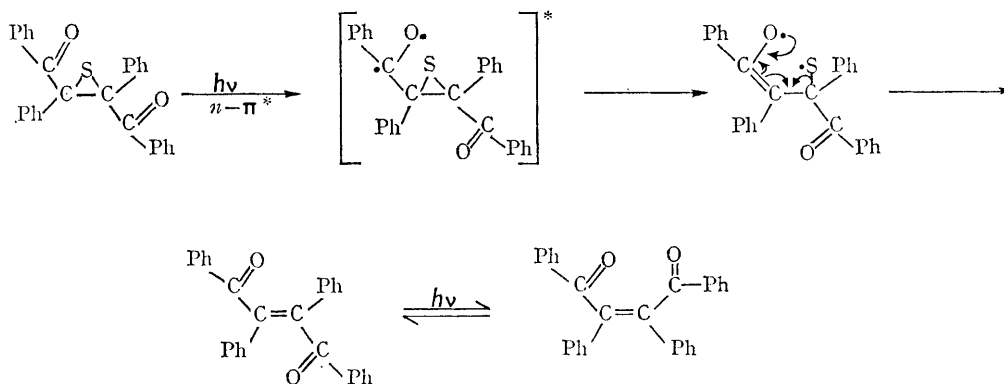
<sup>6</sup> C. O. Guss and D. L. Chamberlain, *J. Amer. Chem. Soc.*, 1952, **74**, 1342.

<sup>7</sup> For a related photo-extrusion of a hetero-atom from a three-membered ring see A. Padwa and L. Hamilton, *J. Amer. Chem. Soc.*, 1965, **87**, 1821.

<sup>8</sup> D. C. Dittmer and G. C. Levy, *J. Org. Chem.*, 1965, **30**, 636.

cleavage of the C $\alpha$ -S bond of the three-membered ring followed by loss of atomic sulphur. The low-energy  $n-\pi^*$  band is undoubtedly the significant absorption band, since light above 290 m $\mu$  was

of the above photoreaction is reminiscent of light-induced fission processes which result in the loss of electronegative substituents from a position  $\alpha$  to the carbonyl group.<sup>9-11</sup> The overall scheme for



employed. The light absorbed by (I) possesses sufficient energy to effect a carbon-sulphur bond cleavage. The driving force for the fission of the episulphide ring can be attributed to the tendency of the excited  $n-\pi^*$  state to eliminate  $\alpha$ -substituents as odd-electron species. The first step

the photolysis of *trans*-dibenzolystilbene episulphide is therefore as given in the diagram.

At this time it is not possible to decide between a concerted one-step extrusion of sulphur from the excited state, or a two-step process in which the photo-extrusion is stereospecific.

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<sup>9</sup> A. N. Strachan and F. E. Blacet, *J. Amer. Chem. Soc.*, 1954, **77**, 5254.

<sup>10</sup> C. Weizmann, Y. Hirshberg, and E. Bergmann, *J. Amer. Chem. Soc.*, 1936, **58**, 1675; 1938, **60**, 1799.

<sup>11</sup> H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *J. Amer. Chem. Soc.*, 1964, **86**, 947.