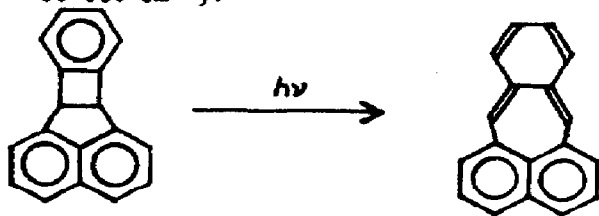


PERICYCLIC REACTIONS IN UPPER SINGLET AND TRIPLET STATES - QUANTITATIVE ASPECTS

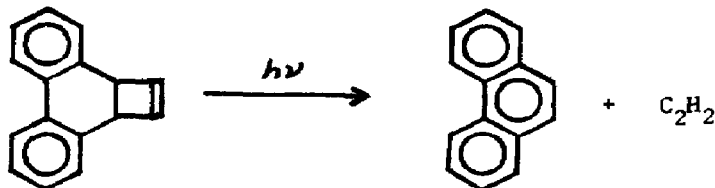
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In organic photochemical reactions in solution it is usually assumed without question that internal conversion and vibrational relaxation to a cool S_1 or T_1 state proceed faster than any chemical transformations. A recent review of wavelength-dependent organic photochemical reactions¹ suggests a range of cases in which this assumption appears questionable. Some of the most convincing cases for reactions from upper singlet and triplet states come from studies of reactions proceeding by successive absorption of two photons. Here we report semi-quantitative results for efficiencies of two pericyclic reactions proceeding in upper excited singlet and triplet states ($45 - 50\,000\text{ cm}^{-1}$):



$$\phi(S_1) = 0, \phi(T_1) = 0, \phi(S_n) \approx 0.01, \phi(T_n) \approx 0.01$$



$$\phi(S_1) = 0, \phi(T_1) = 0, \phi(S_n) \approx 0.01, \phi(T_n) \approx 0.2$$

The implications of these results for mechanistic studies in organic solution photochemistry will be discussed.

(1) N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth, Chem. Rev., 78, 125 (1978).