Photodimerization of Tetramethylethylene. A Reaction of the Olefin π,π^* Singlet

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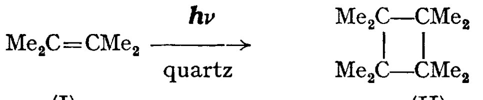
THE dearth of reported examples of the photodimerization of nonconjugated acyclic olefins[1,2] is in marked contrast to that for conjugated and small cyclic olefins[3] where the dimerization usually occurs by way of the triplet obtained by energy transfer from a sensitizer. It is generally believed that the triplet of acyclic olefins is deactivated rapidly, so that the bimolecular dimerization cannot compete. This efficient deactivation pathway is commonly thought to be due to a crossing of the triplet and ground-state potential-energy surfaces which result from the preferred orthogonal conformation of the π,π^* triplet.[4] We report the non-sensitized photodimerization of tetramethylethylene (I) to give octamethylcyclobutane (II).

Neat tetramethylethylene (5·0 ml.), purified by passage through a basic alumina column, was degassed and irradiated in a quartz tube two inches away from a 450w Hanovia medium-pressure Hg lamp. After three weeks the mixture contained *ca.* 30% of (II). The excess of tetramethylethylene was removed from the irradiation mixture by bulb-to-bulb distillation at 0° (8 mm.) and condensation with liquid nitrogen. The residue consisted of *ca.* 75% of (II). Pure octamethylcyclobutane, obtained by preparative v.p.c., is a volatile, crystalline compound (m.p. 198—200°) with a terpene-like odour. The combustion analysis, infrared, n.m.r. [singlet at 0·92 δ ($CDCl_3$); 0·97 δ ($(CD_3)_2CO$] and mass spectrum (parent peak at 168) are all in accord with the structure (II).



(I) (II)

The u.v. spectrum of a concentrated solution of the starting material had no significant absorption at wavelengths longer than 250 mμ, and was essentially the same as that reported.[5] No dimerization occurred with irradiation through a Vycor filter (cut off $\sim$220 mμ). Attempts to sensitize this reaction by means of triplet–triplet transfer using acetophenone (triplet energy 73·6 kcal.), xanthen-9-one (74·2 kcal.), cyclopropyl phenyl ketone (74·3 kcal.) or *m*-xylene ($\sim$85 kcal.) have been unsuccessful. All of these have a triplet energy sufficient to act as sensitizers for the tetramethylethylene triplet since the phosphorescence of acetophenone and cyclopropyl phenyl ketone was quenched by adding tetramethylethylene.

These results indicate that the photodimerization of tetramethylethylene requires direct irradiation into the π,π^* singlet. This implies that the rate of dimerization with the π,π^* singlet of nonconjugated acyclic olefins is fast enough to compete with other deactivation pathways (*i.e.*, intersystem crossing and internal conversion). This is in contrast to the triplet, where deactivation predominates. It is not yet possible to assess the various factors which can influence the rates of these competing processes. It should, however, be pointed out that in the Mulliken model[4c] the π,π^* singlet and ground-state potential-energy surfaces do not cross and thus this efficient deactivation pathway of the triplet may not be available to the singlet.

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