Photocyclodimerization of *p*-Methoxystyrene in the Presence of 1,4-Dicyanobenzene

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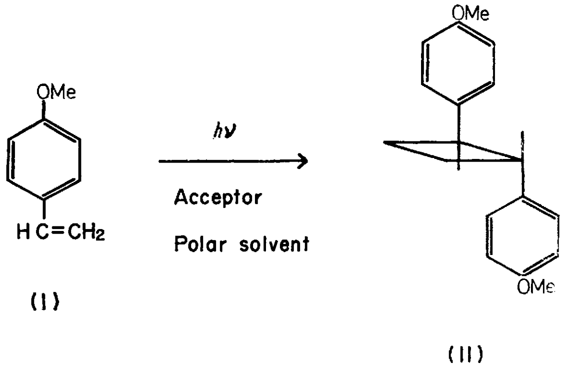
Summary Irradiation of *p*-methoxystyrene in the presence of electron acceptors in polar solvents gives a *trans*-head-to-head cyclodimer of the olefin *via* its cation radical.

Recently the photopolymerization of vinyl compounds by a mechanism involving electron-donor–acceptor (EDA) complexes *e.g. via* exciplex and/or excited EDA complex, has attracted attention.[1] Photocyclodimerization of vinyl compounds in the presence of the electron acceptors or donors, however, has been reported for only a few vinyl compounds, such as *N*-vinylcarbazole,[2] phenyl vinyl ether,[3] and indene.[4] We have found that *p*-methoxystyrene (I) forms a novel cyclodimer *via* its cation radical.

Irradiation of a solution of (I) in acetonitrile (0·66M) in the presence of the electron acceptor *p*-dicyanobenzene with a 300 W high-pressure mercury arc through Pyrex gave the *trans*-head-to-head cyclodimer (II) at a rate of 13% per 10 h, without producing any polymerized material. The product was analysed by gel permeation chromatography. Its mass spectrum showed peaks at *m/e* 268 (M^+) and 134 (100%). The stereochemistry of (II) was assigned on the



basis of its n.m.r. spectrum (C_6D_6; 100 MHz) [δ 2·06 (4H, CH_2), 3·36 (9H, OMe and CH), and 6·72—7·12 (4H + 4H, q, Ph)].

This photocyclodimerization did not occur in non-polar solvents such as benzene and n-hexane, and the presence of an electron acceptor was necessary; in the above system, for example, no photoproduct was obtained without addition of *p*-dicyanobenzene. *o*- and *m*-Dicyanobenzene were also effective electron acceptors for the photocyclodimerization. The emission spectra of (I) in the presence of these electron acceptors were examined in benzene solution. The fluorescence of (I) was quenched by the electron acceptors and a broad exciplex was observed at a longer wavelength region (*ca.* 440 nm) than that for the normal fluorescence of (I). Stern–Volmer plots for the fluorescence quenching by the dicyanobenzenes were all linear with a slope (quenching constant: $k_q\tau_0$) of 265 l/mol (for *p*-dicyanobenzene), 168 (*o*), and 90 (*m*), respectively. The effects of electron acceptors which form ground state EDA complexes with (I), such as 1,3,5-trinitrobenzene, 2,4,7-trinitrofluorenone and 1,2,4,5-tetracyanobenzene, were also examined by excitation of their charge-transfer bands. Tetracyanobenzene induced photocyclodimerization of (I) in solution but the two former acceptors suppressed the photocyclodimerization and initiated polymerization of (I).

It is known for EDA systems that excited electron-donor molecules may transfer an electron to the acceptor in polar media, forming solvated ion radicals, whose exciplex emission can be observed in some cases. The above results can be explained in terms of an intermediate cation radical of (I) by a mechanism[5] involving a photochemical electron transfer resulting in formation of styrene cation radical which adds electrophilically to the β carbon of another ground-state styrene molecule, and subsequent cyclodimerization to cyclobutane dimer cation. The cyclobutane dimer cation would be neutralized by back electron transfer from an acceptor anion radical and the cyclobutane dimer would be formed.

$$\begin{tikzcd}
(\mathrm{I}) \arrow[r, "h\nu"] & (\mathrm{I})^* \arrow[r, "\text{Acceptor}", "\text{in polar solvents}"'] & (\mathrm{I})\ \text{Cation radical} + \text{Acceptor anion radical} \arrow[d, "(\mathrm{I})"] \\
& & (\mathrm{II})\ \text{Cation radical} \arrow[d, "\text{Acceptor anion radical}"] \\
& & (\mathrm{II})
\end{tikzcd}$$

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[5] This mechanism is analogous to that proposed by Ledwith for *N*-vinylcarbazole dimerization. See A. Ledwith, *Accounts Chem. Res.*, 1972, **5**, 133.