Photosensitized Cyclodimerization of Phenyl Vinyl Ether

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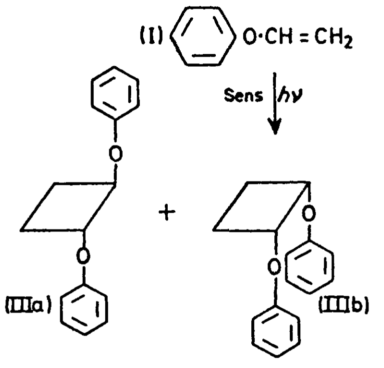
Summary Irradiation of phenyl vinyl ether in the presence of aromatic compounds, such as dimethyl terephthalate, methyl benzoate, or benzonitrile, gives a mixture of *trans*- and *cis*-head-to-head cyclodimers of the olefin.

The photocyclodimerization of olefins with or without a sensitizer has received attention, especially from the synthetic point of view.[1] The dimerization of vinyl ethers, however, has not yet been reported. During our study on the photochemical reactions of aromatic esters,[2] we found a novel dimerization of vinyl ethers in the presence of an aromatic ester. We describe here the dimerization of phenyl vinyl ether (I) which proceeds through an exciplex between a photoexcited sensitizer and the ether (I).



Irradiation of an acetonitrile solution of the ether (I) (0·050 mol) and dimethyl terephthalate (II) (0·021 mol) with a 500 W high pressure mercury arc through a Pyrex filter gave a mixture of *trans*- and *cis*-head-to-head cyclodimers [(IIIa), m.p. 67·5—68·5° and (IIIb) m.p. 80—80·5°] in 30% yield based on the olefin which had reacted (isomer ratio, 3:4).† In the presence of methyl benzoate or benzonitrile the photodimerization of (I) gave the dimers (IIIa) and (IIIb). Ethyl vinyl ether, which has no absorption in the long wavelength region, also underwent dimerization in the presence of the ester (II) to give head-to-head dimers. In the absence of sensitizer dimers were not obtained. This indicates that the aromatic compounds sensitize the dimerization. In order to elucidate the mechanism the quenching of the fluorescence of the ester (II) was examined. The fluorescence of (II) (λ_{max} *ca.* 380 nm) was easily quenched by the olefin (I), and the Stern–Volmer plots of F_0/F against the concentration of the ether (I) were linear (slope, 20 l mol^{-1}). An exothermic singlet-singlet energy transfer from the ester (II) to the ether (I) is not responsible for the quenching, because the fluorescence spectrum of compound (I) showed the maximum at 309 nm. Furthermore, the u.v. absorption spectrum of a mixture of compounds (I) and (II) showed no new absorption band. This excludes the formation of a ground-state charge-transfer complex between compounds (I) and (II). Thus, the dimerization of the olefin (I) may proceed through a complex formed between the π–π* excited singlet state of (II) and the ground state of (I) [equation (1)].

$$(\mathrm{II}) \xrightarrow[\pi-\pi^*]{h\nu} [\mathrm{II}]S_1 \xrightarrow{(\mathrm{I})} [\mathrm{Complex}] \xrightarrow{(\mathrm{I})} (\mathrm{IIIa}) + (\mathrm{IIIb}) \qquad (1)$$

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† Satisfactory analytical data were obtained. The structures were confirmed by mass and n.m.r. spectra.

‡ The fluorescence of the ester (II) derives from a π–π* transition.[2]

[1] D. C. Neckers, 'Mechanistic Organic Photochemistry', Reinhold, New York, 1967, p. 98.

[2] Y. Shigemitsu, Y. Katsuhara, and Y. Odaira, *Tetrahedron Letters*, 1971, 2887.