Photocyclodimerization of *p*-(*NN*-Dimethylamino)styrene

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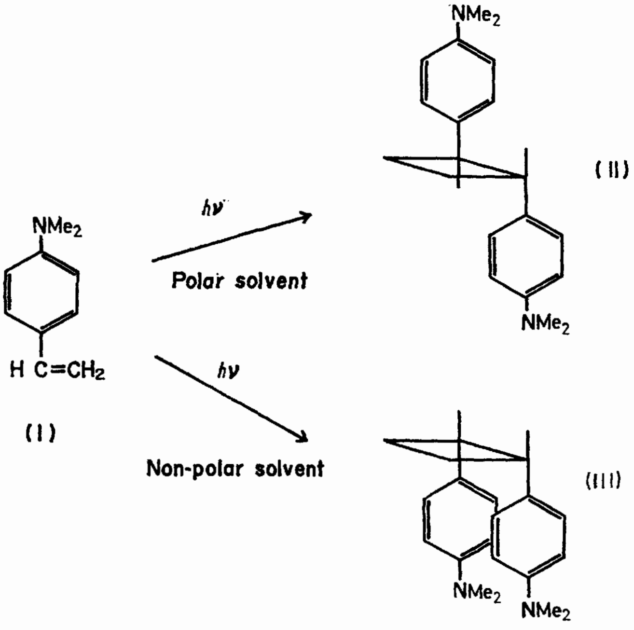
Summary U.v. excitation of *p*-(*NN*-dimethylamino)styrene produces the 1,2-*cis*-cyclodimer in non-polar solvents, whereas the 1,2-*trans*-cyclodimer is obtained in polar solvents.

In the preceding communication,[1] the photocyclodimerization of electron-donating vinyl compounds such as *p*-methoxystyrene in the presence of electron acceptors was reported. In the course of photocyclodimerization of various vinyl compounds, we found that on u.v. excitation *p*-(*NN*-dimethylamino)styrene (I) also gives the cyclobutane dimer, but in this case electron acceptors are not necessary. Further, the cyclodimer is produced irrespective of solvent polarity, but the stereochemistry of the cyclodimer depends on the solvent polarity, *i.e.*, the 1,2-*cis*-cyclobutane is formed in non-polar solvents and the *trans*-isomer in polar solvents.

Irradiation of an acetonitrile solution of (I) (0·66M) with 300 W high-pressure mercury arc through a glass filter (cut-off wavelength 325 nm) gave the *trans*-head-to-head cyclodimer (II), m.p. 95—96 °C at a rate of 0·81% per h together with polymer at a rate of 0·35% per h. The mass spectrum of (II) shows peaks at *m/e* 294 (M^+), 266, and 134 (100%),[2] n.m.r. spectrum peaks at δ (C_6D_6; 100 MHz) 2·18 (4H, m, CH_2), 2·57 (12H, s, Me), 3·50 (2H, CH), and 6·68—7·25 (8H, q, Ph). This photocyclodimerization occurs in various polar solvents such as benzonitrile and dimethylformamide, by a similar mechanism to that for *p*-methoxystyrene and *N*-vinylcarbazole, *i.e.*, *via* its cation radical as an intermediate.[1] The photochemical formation



of the cation radical of (I) was confirmed by flash spectroscopy [(I): 1×10^{-3} M in PhCN solution]. Transient spectra after 100 μs show peaks at 650s, 590s, and 450—540 nm, which can be assigned to the cation radical by comparison with the results of γ-irradiation of (I) in Bu^sCl rigid matrix.[3] The photocyclodimerization of (I) is different from that of the other vinyl monomers so far examined by the fact that the photoexcitation of (I) is sufficient for the reaction, i.e., even without an electron acceptor photoexcitation of (I) produces its cation radical, since (I) has lower ionization potential than *p*-methoxystyrene or *N*-vinylcarbazole.[4] This scheme is quite different from the 'excited triplet state,' mechanism that has been established for the photochemical formation of cyclobutanes from mono-olefins.[5]

U.v. irradiation of a solution of (I) in benzene or n-hexane (0·66 M) gave another product, whose structure was assigned to the *cis*-head-to-head cyclobutane dimer (III) by its mass [*m/e* 294 (M^+), 266, and 134 (100%)[2]] and n.m.r. spectrum [δ(C_6D_6; 100 MHz) 2·42 (16H, CH and Me), 3·88 (2H, CH), and 6·42—7·02 (8H, q, Ph)].

It is interesting that the structure of the cyclobutane dimer of (I) depends on the solvent polarity; the *trans*-head-to-head cyclodimer is obtained in polar solvents whereas the *cis*-head-to-head cyclodimer is formed in non-polar solvents. The *cis*-dimer may be formed *via* a cation dimer which is formed between a cation radical of (I) and the ground state (I) or through an excimer of (I).

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[1] M. Yamamoto, T. Asanuma, and Y. Nishijima, *J.S.C. Chem. Comm.*, 1974, 53.

[2] M. L. Gross and C. L. Wilkins, *Tetrahedron Letters*, 1969, **44**, 3875.

[3] To be published. See T. Shida and W. H. Hamill, *J. Chem. Phys.*, 1966, **44**, 2375 for this method.

[4] The ionization potentials of *p*-aminostyrene, *p*-methoxystyrene, and carbazole are 7·55, 7·92, and 7·68 eV, respectively. The first two are adiabatic I.P.s determined from the CT band: M. Hatano, N. Tamura, and S. Kambara, *J. Chem. Soc. Japan, Ind. Chem. Section*, 1967, **70**, 2012, and the third is a vertical I.P. obtained by photoelectron spectroscopy: H. J. Haink, J. E. Adams, and J. R. Huber, *Ber. Bunsengesellschaft Phys. Chem.*, 1974, **78**, 436. Hence the ionization potential of *p*-(*NN*-dimethylamino)styrene is much smaller than 7·55 eV.

[5] *Cf.* D. J. Trecker, 'Organic Photochemistry,' vol. 2, ed. O. L. Chapman, Marcel Dekker, New York, 1969, p. 63.