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MARKED DEPENDENCE OF MULTIPLICITY IN DIRECT Z,E PHOTOISOMERIZATION OF A SERIES OF METHYL CINNAMATES ON THEIR PARA-SUBSTITUENTS

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Direct Z,E photoisomerization has extensively been studied with a large number of olefins, particularly with stilbenes.[1] Bent and Schulte-Frohlinde[2] have shown that the addition of a small amount of azulene or ferrocene makes it possible to alter the positions of the photostationary states for direct isomerization of stilbenes possessing the p-nitro groups, known to enhance intersystem crossing. Here we report the marked dependence of multiplicity in the direct E→Z photoisomerization of a series of methyl cinnamates on their para-substituents ——— *via* the triplet state for electron-withdrawing substituents and *via* the singlet state for electron-donating ones.

A typical execution of this photoisomerization is as follows. A solution of methyl p-nitro-(E)-cinnamate (0.5 mmol) in dry acetonitrile (100 cm^3) was placed in a quartz vessel and irradiated with a 100 watt high-pressure mercury arc under argon at 10 °C. An identical parallel experiment was set up at the same concentration as with methyl p-nitro-(Z)-cinnamate. The two tubes were irradiated equidistant from the light source. The progress of the reactions (Z/E ratio) was monitored by the examination of aliquots by glpc.

As can be seen from Table 1, the photostationary state had no close relation to the wavelength λ_{max} (a measure of relative singlet excitation energy)[3] or to the ratio ($\varepsilon_E/\varepsilon_Z$) of molar extinction coefficient (ε) at the maximal absorption. With (E)-cinnamic acid,[4] however, a relationship has been reported to exist

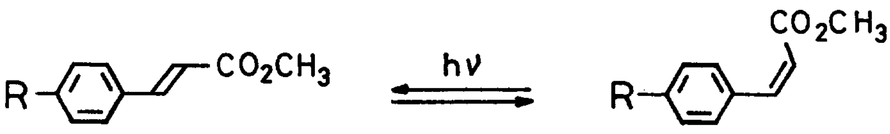

Table 1. UV Absorption and Photostationary States of p-Substituted Methyl Cinnamates.

Substituent R	UV Absorption λ_{max}, nm ($\varepsilon/10^4M^{-1}cm^{-1}$) Z-Isomer	E-Isomer	Photostationary (Z/E) Value[a] 0.005M	0.05M	0.05M (FcH Added)[b]
O_2N	298 (1.45)	303 (2.01)	1.69	1.42	0.09
NC	271 (1.54)	283 (3.10)	2.10	1.46	0.62
CH_3CO	281 (1.75)	291 (3.00)	2.20	1.22	0.10
Cl	-----	282 (2.47)	1.94	1.78	1.81
H	267 (0.97)	276 (2.16)	1.52	1.50	1.50
CH_3	-----	286 (2.32)	2.07	1.70	2.15
$(CH_3)_2CH$	283 (1.12)	286 (2.43)	2.03	1.60	1.90
CH_3O	301 (1.33)	309 (2.34)	1.20	0.81	1.30
$(CH_3)_2N$	-----	362 (2.61)	0.55	0.40	0.34

[a] Acetonitrile solutions were irradiated with a 100 watt high-pressure mercury arc under argon and the Z/E ratios were determined by glpc.
[b] One mole equivalent of ferrocene coexisted in the solution.

between the photostationary state and the $\varepsilon_E/\varepsilon_Z$ ratio in the 313-nm irradiation. Since the $\varepsilon_E/\varepsilon_Z$ ratio at any wavelengths for a series of p-substituted methyl cinnamates does not reflect the photostationary state (Table 1), the Z/E ratio could, therefore, be correlated with the difference in the decay ratio (k_Z/k_E) from the S_1 or T_1 state into each isomer. The relatively low E→Z isomerization efficiency for methyl p-dimethylamino-(E)-cinnamate may be ascribed to the torsional conversion barrier between the vibrationally relaxed singlet state of E-form and a twisted excited singlet state.

We then studied effects of ferrocene and azulene (well-known good triplet quenchers) on the positions of the photostationary states of a series of p-substituted methyl cinnamates, using a 0.05 $mol{\cdot}dm^{-3}$ acetonitrile solution under argon (Table 1). As a result, both the quenchers strongly decreased the Z/E ratio in the photostationary state of methyl cinnamate having the nitro, acetyl, or cyano group at the para-position of its benzene ring. On the other hand, for methyl cinnamate with the methyl, isopropyl, or methoxyl group as its para-substituent, the presence of one mole equivalent of ferrocene rather caused a slight increase in the Z/E ratio for these substituted methyl cinnamates (Fig. 1)

With unsubstituted, p-chloro-, and p-dimethylaminocinnamic acid methyl esters, the addition of ferrocene has been found to produce no significant changes in the Z/E ratio.

Fig. 2 illustrates a plot of the Z/E ratio for methyl p-nitrocinnamate both in the presence and absence of ferrocene against the irradiation time, equilibrium being approached from both the Z and E sides. The Z/E ratio without the triplet quenchers reached a minimum value at 20 min irradiation and then exhibited a progressive increment with the irradiation time. This phenomenon can probably be explained as resulting from a decrease in the amount of Z- and E-olefins, caused by the photodimerization[5] competing with the photoisomerization The photostationary Z/E ratio for methyl p-nitrocinnamate under argon was 1.67, 1.58, 1.47, and 1.42 for the 0.01, 0.025, 0.04, and 0.05 mol·dm^{-3} acetonitrile solution, respectively. Furthermore, the data in Fig. 3, where [E]/[Z] was plotted against [ferrocene] in an argon-saturated acetonitrile solution, showed that the slope/intercept ratio for both 30 and 180 min irradiations was 380 —— the value was far larger than might be expected for the singlet quenching (nearly zero to 15).[1b]

It may be concluded from these results that (1) with p-nitro-, p-acetyl-,

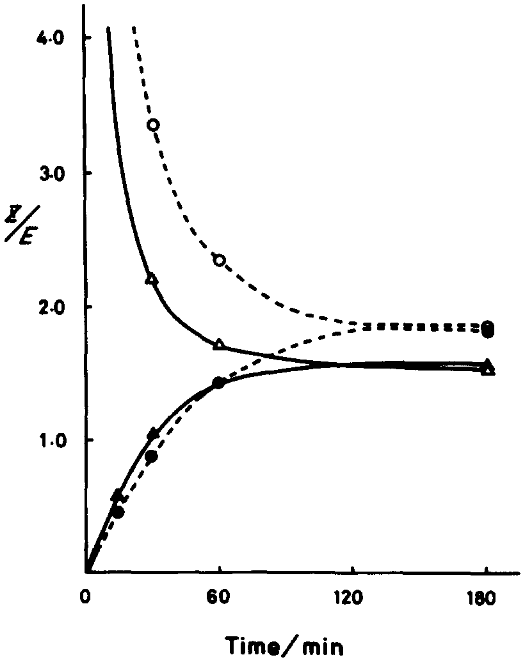

Fig. 1 Photoisomerization of methyl p-isopropyl-(E)-cinnamate in the presence (●,○) and absence (▲,△) of ferrocene.

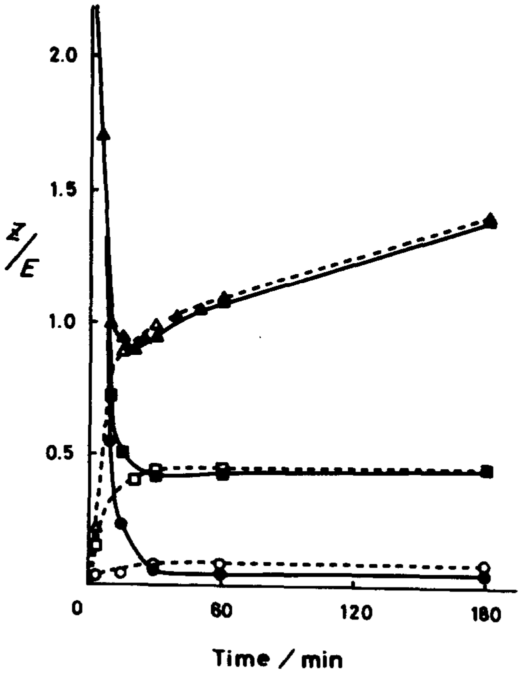

Fig. 2 Photoisomerization of methyl p-nitro-(E)-cinnamate in the presence [0.1 eq (■,□); 1.0 eq (●,○)] and absence (▲,△) of ferrocene.

and *p*-cyanocinnamic acid methyl esters the *E*→*Z* isomerization takes place *via* the triplet state, whereas the *Z*→*E* isomerization occurs *via* the singlet state with no triplet transient being practically produced from excitation of the *Z* form and (2) with the other methyl cinnamates (*p*-isopropyl, *p*-methyl, *p*-methoxyl, *p*-chloro, and unsubstituted ones), *E*→*Z* and *Z*→*E* isomerizations seem to occur *via* the excited singlet state of each isomer. This observation is in accord with the singlet state mechanism now accepted for the direct isomerization of cinnamic acid itself.[6]

The elucidation of the reason why the excited multiplicities of this *Z*,*E* photoisomerization vary will be the subject of further investigation.

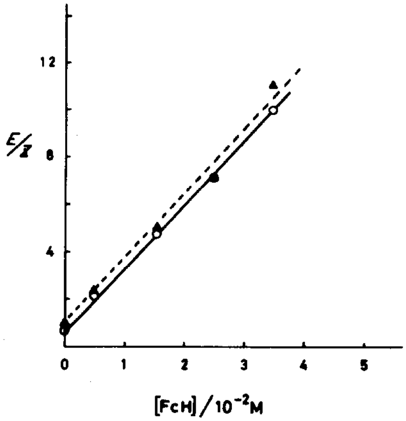

Fig. 3 The effect of ferrocene on photostationary ratio of methyl *p*-nitrocinnamate for 30 min (▲) and 180 min (○) irradiations.

REFERENCES AND FOOTNOTES

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(b) J. Saltiel and E. D. Megarity, *ibid.*, **94**, 2742 (1972).

2) D. V. Bent and D. Shulte-Frohlinde, *J. Phys. Chem.*, **78**, 451 (1974).

3) The order of bathochromic displacements for *para*-substituted (*E*)-isomers was Cl (+6) < CN (+7) < CH_3, $(CH_3)_2CH$ (+10) < CH_3CO (+15) < NO_2 (+27) < CH_3O (+33) < $(CH_3)_2N$ (+86). The large shift observed with *p*-dimethylamino-(*E*)-cinnamate would be due to the contribution of intramolecular charge-transfer.

4) M. B. Hocking, *Can. J. Chem.*, **47**, 4567 (1969).

5) The yields of photodimers of methyl *p*-nitro-(*E*)-cinnamate were reported to be 2 and 61% for 20 and 180 min irradiation, respectively, in acetonitrile. See, T. Ishigami, T. Murata, and T. Endo, *Bull. Chem. Soc. Jpn.*, **49**, 3578 (1976).

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