Stereochemistry of the Cycloaddition of Singlet Excited β-Substituted Styrenes to Olefins[1]

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The photocycloaddition of β-substituted styrenes (*trans*-cinnamic acid (**1***b*), methyl *trans*-cinnamate (**1***c*), *trans*-cinnamonitrile (**1***d*), and *cis*-cinnamonitrile) to olefins occurs with retention of stereochemistry and involves the S_1 state. In certain cases (**1***b*, *c*) a photoene reaction competes with the cycloaddition. The triplet states of the β-substituted styrenes produced by sensitization give only *cis* ⇄ *trans* isomerization. Neither cycloadduct nor photoene reaction is observed from the triplet states. It is thus likely that both addition and photoene reactions involve the S_1 state of the β-substituted styrene.

La photocycloaddition des styrènes β substitués (acide *trans* cinnamique (**1***b*), cinnamate de méthyle *trans* (**1***c*), cinnamonitrile *trans* (**1***d*), et cinnamonitrile *cis*) aux oléfines se fait avec rétention de stéréochimie et passe par l'état S_1. Dans certains cas (**1***b*, *c*) la réaction photoène entre en compétition avec la cycloaddition. Les états triplets des styrènes substitués obtenus par sensibilisation, ne conduisent qu'à l'isomérisation *cis* ⇄ *trans*. La cycloaddition ainsi que la réaction photoène n'ont pas été observées à partir des états triplets. Il est donc probable que la réaction photoène et l'addition passent toutes deux par l'état S_1 du styrène β substitué.

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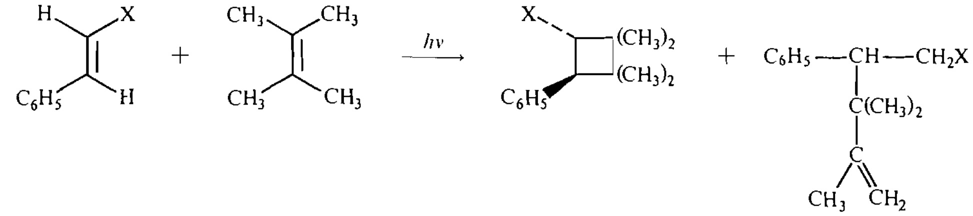
The mechanism of the photocycloaddition of *trans*-stilbene to tetramethylethylene involves reversible reaction of S_1 *trans*-stilbene with ground state tetramethylethylene giving an exciplex which demotes to the adduct with retention of the *trans*-stereochemistry (1). We now report that photocycloaddition of other β-substituted styrenes (**1***b*–*d*) occurs with retention



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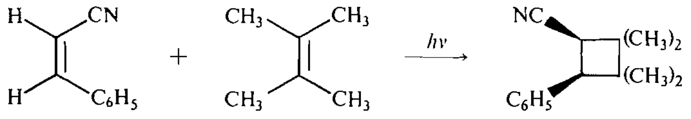
a, X = C_6H_5; *b*, X = CO_2H; *c*, X = CO_2CH_3; *d*, X = CN



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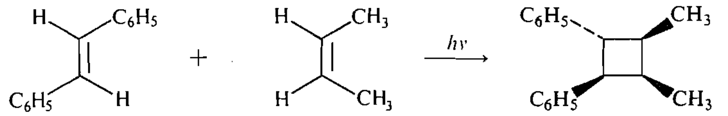

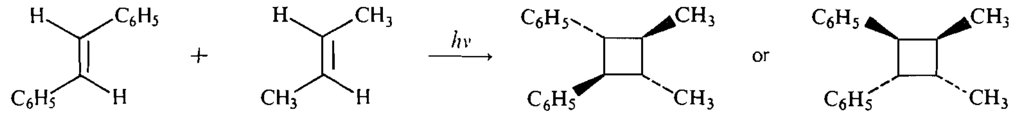

of stereochemistry and involves the S_1 state. In certain cases (**1***b*, *c*) a photoene reaction competes with the cycloaddition. The triplet states of the β-substituted styrenes produced by sensitization give only *cis* ⇄ *trans* isomerization. Neither cycloadduct nor photoene reaction is observed from the triplet states. It is thus likely that both addition and photoene reactions involve the S_1 state of the β-substituted styrene.[5]

Irradiation of benzene solutions of *trans*-stilbene (**1***a*), *trans*-cinnamic acid (**1***b*), methyl *trans*-cinnamate (**1***c*), and *trans*-cinnamonitrile (**1***d*) in the presence of tetramethylethylene give in each case an adduct (**2**) in which the *trans*-stereochemistry is maintained.[6] The corresponding *cis*-β-substituted styrenes, with the exception of *cis*-cinnamonitrile, do not add to tetramethylethylene sufficiently rapidly to compete effectively with *cis* → *trans* isomerization. Irradiation of *cis*-cinnamonitrile in the presence of tetramethylethylene gives an adduct in which the phenyl and nitrile groups are *cis*. Both *trans*- and *cis*-cinnamonitrile give linear $1/\Phi_{\text{add}}$ *vs.* 1/[olefins] plots. Irradiation of solutions of either nitrile and sensitizers (benzophenone, 2-acetylnaphthalene)[7] gives only *cis* ⇄ *trans* isomerization. The cycloaddition of these S_1 β-substituted styrenes is stereospecific with respect to the excited enophile.

Irradiation of *trans*-stilbene in the presence of *cis*-2-butene gives a single adduct which shows two methyl resonances in the n.m.r. spectrum.[8] In similar fashion, *trans*-stilbene in the presence of *trans*-2-butene gives a single, different adduct in which the n.m.r. spectrum shows equivalent methyl groups.[8] These photocycloadditions clearly occur with retention of stereochemistry on both the excited (S_1) enophile and the ground state olefin.

In the irradiation of *trans*-cinnamic acid and methyl *trans*-cinnamate in the presence of tetramethylethylene a second product was obtained in addition to the cycloadduct (**2**). The additional product in each was shown to be the terminal olefin expected from a photoene reaction to which we tentatively assign structure **3***b*, *c*. The ratio of cycloadduct to photoene product in neat tetramethylethylene was **2***c*/**3***c* = 1.5 and in benzene **2***b*/**3***b* = 5 and **2***c*/**3***c* = 1.6. In the other cases studied (**1***a* and *d*) photoene products were not observed. Polar solvents favored the photocycloaddition to a small extent (**2***c*/**3***c* = 3.2 in ethanol and 3.4 in acetic acid). The ratio of cycloadduct to photoene was insensitive to variation in light intensity. In the

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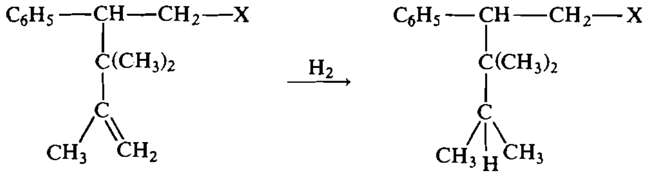
[5] The fact that the triplet states do not give either the adduct or the photoene is consistent with reaction via either S_1 or vibrationally excited S_0. Rapid thermal equilibration of vibrationally excited species in solution makes reaction of an S_0 state unlikely. Furthermore, it has been shown that cycloaddition of *trans*-stilbene involves the S_1 state (1).

[6] Irradiations were carried out with a 450 W Hanovia medium pressure mercury vapor lamp through a Pyrex filter. The adducts all gave satisfactory element analyses and spectra consistent with the cyclobutane adduct structures (**3***b*–*d*). Saponification of the adduct from methyl *trans*-cinnamate gave the adduct (m.p. 129–130°) from *trans*-cinnamic acid. This adduct was converted by methyl lithium to the corresponding methyl ketone. The ketone did not epimerize under conditions which led to exchange of four protons for deuterium and hence must have the thermodynamically more stable *trans* arrangement of phenyl and acetyl groups. Oxidation of the methyl ketone gave the adduct from *trans*-cinnamic acid which thus must have *trans* phenyl and carboxyl groups. The adduct from *trans*-cinnamic acid was converted via the amide to the nitrile which was identical to the adduct obtained from *trans*-cinnamonitrile.

[7] The irradiation of solutions of 2-acetylnaphthalene with methyl cinnamate under these conditions leads to the adduct described previously (2).

[8] The adduct from *cis*-2-butene shows n.m.r. bands at δ 7.25 (10H, aromatic protons), 3.2–4.0 (2H, benzyl methine protons), 2.2–2.9 (2H, m, methine protons), 1.15 (3H, d, methyl protons), and 0.80 (3H, d, methyl protons). The adduct from *trans*-2-butene shows n.m.r. bands at δ 7.20 (10H, aromatic protons), 4.10 (2H, m, benzyl methine protons), 2.1–2.5 (2H, m, methine protons), and 0.95 (6H, d, methyl protons).



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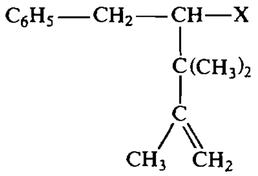

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sensitized reactions neither cycloadduct nor photoene was observed. Heating methyl *trans*-cinnamate with tetramethylethylene at 200° for 24 h gave no detectable reaction.

The tentative structural assignment (**3***b*, *c*) for the photoenes rests primarily on the n.m.r. spectrum. The alternative structure **6** has not been rigorously excluded. The n.m.r. spectrum of the photoene (m.p. 114.5–115.5°) from *trans*-cinnamic acid shows non-equivalent methyl groups (δ 0.82 and 0.95), a vinyl methyl group (δ 1.78), and ABX pattern for the methylene and methine protons (AB centered at δ 2.51, X at 3.21), terminal methylene protons (δ 4.72), aromatic protons (5, δ 7.33), and a carboxyl proton (δ 11.25). The mixture of esters (**2***c* and **3***c*) from methyl *trans*-cinnamate is difficult to separate, but hydrolysis of the mixture and repeated crystallizations from heptane gave the acids **2***b* (25%) and **3***b*(7%). Catalytic reduction of the mixture of esters and v.p.c. separation gave **7***c*.

The demonstration that singlet addition of β-substituted styrenes to tetramethylethylene is a general phenomenon, the demonstration that the photocycloaddition of S_1 *trans*-stilbene to tetramethylethylene proceeds via an exciplex (1), and the demonstration that these photocycloadditions are stereospecific on both the excited enophile and the ground state olefin place stringent limits on the mechanisms which can be considered. The most probable mechanism is concerted decay of an exciplex to the adduct. If an intermediate such as a singlet 1,4-biradical is formed, the lifetime of this intermediate must be short with respect to the reciprocal of the rate constant for rotation about a single bond. This seems unlikely in view of the known behavior of singlet 1,4-biradicals (3, 4). It may be that unsymmetrically substituted olefins or olefins with radical stabilizing substituents will favor formation of long-lived biradicals. Studies directed to this point are in progress.

The stereospecificity of the addition of singlet excited styrenes to olefins together with the observed retention of stereochemistry in the dimerization of the isomeric 2-butenes upon direct irradiation (5) suggests that singlet cycloaddition may provide a useful tool for stereospecific synthesis of complex molecules.

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