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UNUSUAL BEHAVIOUR OF β-tert-ALKYLSTYRENES IN PHOTOSENSITIZED CIS-TRANS ISOMERIZATION. STRUCTURAL EFFECTS ON TRIPLET ENERGY TRANSFER

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Photostationary state isomer ratios, rate constants for triplet energy transfer, and quantum yields of isomerization were determined for the triplet sensitized isomerization of β-alkylstyrenes (PhCH=CHR, R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, and $C(CH_3)_2CH_2CH_3$) in benzene. The remarkably high ratio of cis-tert-alkylstyrenes at the photostationary state is mainly attributed to lower rate constants for energy transfer to cis-isomers than to trans-isomers.

We report new results pertaining to triplet sensitized cis-trans isomerization of β-alkylstyrenes. These olefins have not received much attention[1] despite of many studies of photochemical isomerization of olefins over the past years.[2]

A solution of cis- and/or trans-β-alkylstyrenes in benzene was irradiated[3] at 366 nm in the presence of triplet sensitizers of varying triplet excitation energies[4] (cf. Fig. 1) at ambient temperature. The resulting isomerization mixture was examined by vpc to determine the photostationary state isomer ratios. Figure 1 shows the results obtained by extrapolation to infinite dilution with respect to sensitizer concentration. The curves in Figure 1 show that the photostationary state compositions of β-methyl-, β-ethyl-, and β-isopropylstyrene are quite similar to that of stilbene[5] and confirm a strong similarity in mechanism between photosensitized isomerization of these alkylstyrenes and stilbene. On the other hand, the photostationary state compositions of β-tert-butyl- and β-tert-amylstyrene are quite different from the former case and the cis isomer ratios are remarkably high for all sensitizers employed. From the profiles in Figure 1 triplet excitation energies of the olefins are estimated[5] to be ca. 62 kcal/mol for cis-isomers and ca. 56 kcal/mol for the trans-isomers of β-methyl-,[6] β-ethyl-, and β-isopropylstyrene, and ca. 70 kcal/mol for the cis-isomers and ca. 60 kcal/mol for the trans-isomers of β-tert-butyl- and β-tert-amylstyrene.

The photosensitized isomerization is assumed, by analogy with stilbene isomerization, to proceed through the following processes,

$$\mathrm{S} \longrightarrow {}^{1}\mathrm{S}^{*} \xrightarrow{\phi_{isc}} {}^{3}\mathrm{S}^{*}$$

$${}^{3}\mathrm{S}^{*} \xrightarrow{k_{sd}} \mathrm{S}$$

$${}^{3}\mathrm{S}^{*} + \text{t-AS} \xrightarrow{k_{st}} \mathrm{S} + {}^{3}\mathrm{AS}^{*}$$

$${}^{3}\mathrm{S}^{*} + \text{c-AS} \xrightarrow{k_{sc}} \mathrm{S} + {}^{3}\mathrm{AS}^{*}$$

$${}^{3}\mathrm{AS}^{*} \xrightarrow{k_{t}} \text{t-AS}$$

$${}^{3}\mathrm{AS}^{*} \xrightarrow{k_{c}} \text{c-AS}$$

where S and AS stand for a sensitizer and a β-alkylstyrene, respectively, and k's refer to specific rate constants for the corresponding processes. The photostationary state composition is expressed by eq. 1 and quantum yields of the isomerization by eq. 2. In order to shed light on the source of the aforementioned high

$$\left.\frac{[\text{c-AS}]}{[\text{t-AS}]}\right|_{pps} = \frac{k_{st}}{k_{sc}} \frac{k_{c}}{k_{t}} \tag{1}$$

$$\phi_{t\to c} = \phi_{isc} \frac{k_{st}[\text{t-AS}] + k_{sc}[\text{c-AS}]}{k_{sd} + k_{st}[\text{t-AS}] + k_{sc}[\text{c-AS}]} \frac{k_{c}}{k_{t} + k_{c}} \tag{2c}$$

$$\phi_{c\to t} = \phi_{isc} \frac{k_{st}[\text{t-AS}] + k_{sc}[\text{c-AS}]}{k_{sd} + k_{st}[\text{t-AS}] + k_{sc}[\text{c-AS}]} \frac{k_{t}}{k_{t} + k_{c}} \tag{2t}$$

ratio of the cis-isomer of the tert-alkylstyrenes, rate constants for excitation transfer from benzophenone and chrysene to β-methylstyrenes and β-tert-butylstyrenes were determined by quenching of phosphorescence of benzophenone using single photon counting technique and quenching of triplet-triplet absorption of chrysene using a flash photolysis apparatus.[8] The measured rate constants are summarized in Table 1. In the case of β-methylstyrenes, benzophenone (E_T = 68.6 kcal/mol)[4] transfers excitation energy to both isomers at nearly diffusion controlled rates; however, excitation transfer from chrysene (E_T = 56.6 kcal/mol)[4] is much slower than diffusion controlled and the rate constant for excitation transfer to the cis-isomer is six times smaller than to the trans-isomer. As for excitation transfer to β-tert-butylstyrenes, even when benzophenone was used as a sensitizer, the rate constant for the cis-isomer is about ten times smaller than that for the trans-isomer. The magnitude of the rate constants is in good agreement with the estimate of the triplet excitation energies of the olefins and suggest that the remarkably high composition of the cis-isomer of β-tert-butylstyrene at the photostationary state is due to the slower energy transfer rate from the sensitizers to cis-tert-butylstyrene.[9]

Table 2 shows isomerization quantum yields determined at low conversion (<8%) by irradiating[11] benzene solutions of β-tert-butylstyrene in the presence of benzophenone or 2-acetylnaphthalene (E_T = 59.4 kcal/mol)[4] as a sensitizer

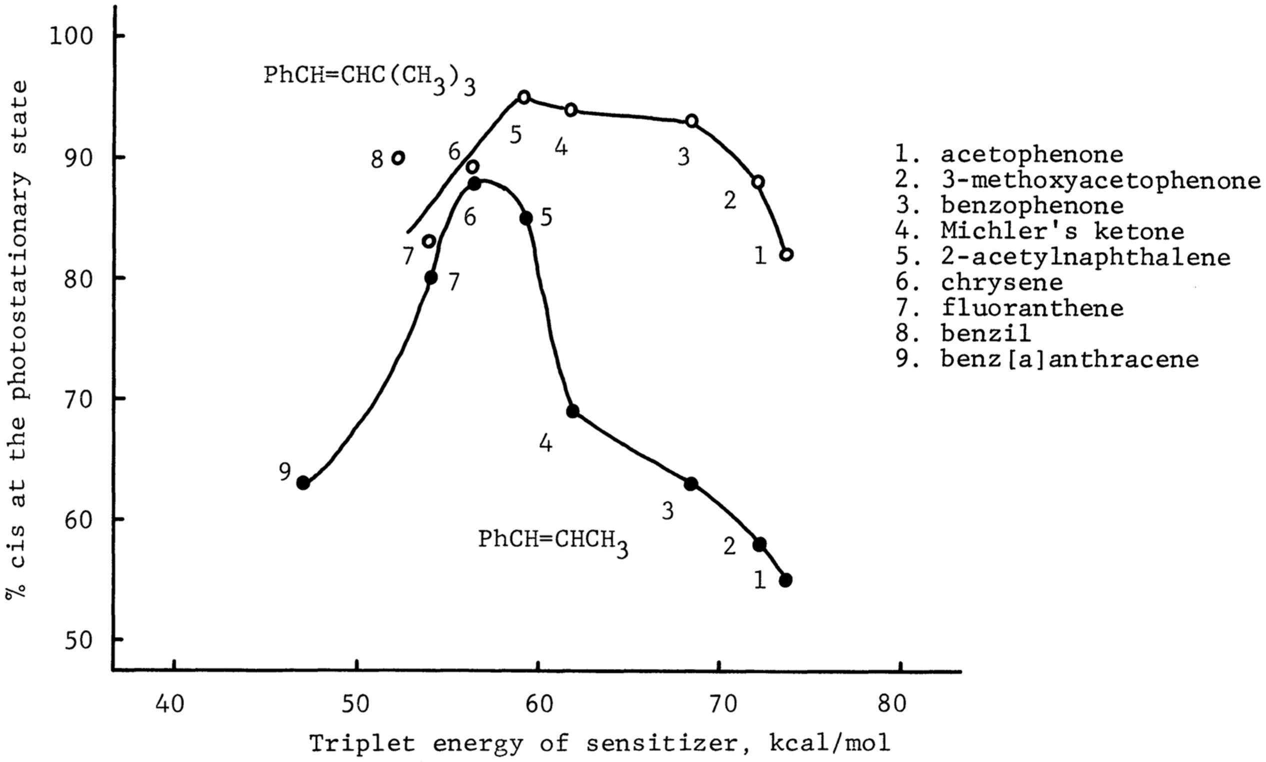

Figure 1. Photostationary State Composition in Triplet Sensitized Isomerization of β-Alkylstyrenes at Ambient Temperature in Benzene. The curves for β-ethyl-, β-isopropyl-, and β-tert-amylstyrene are omitted for simplicity (see the text).

Table 1. Rate Constants for Triplet Excitation Transfer

Sensitizer	R in PhCH=CHR	k_{st}, $M^{-1}s^{-1}$	k_{sc}, $M^{-1}s^{-1}$
Benzophenone	CH_3	1.95×10^9	1.21×10^9
	$C(CH_3)_3$	1.21×10^9	1.25×10^8
Chrysene	CH_3	5.4×10^7	8.8×10^6
	$C(CH_3)_3$	1.1×10^7	6.2×10^5

Table 2. Quantum Yields for Isomerization of β-tert-Butylstyrene

Sensitizer	Concentration (M)		$\phi_{t\to c}/\phi_{isc}$	$\phi_{c\to t}/\phi_{isc}$
	Sensitizer	Butylstyrene		
Benzophenone	0.10	0.02	0.53	0.23
	0.10	0.05	0.55	0.25
2-acetylnaphthalene	0.35	0.02	0.48	0.094
	0.35	0.05	0.49	0.15
		∞		0.24[a]

[a] Quantum yield extrapolated to infinite olefin concentration.

at ambient temperature using benzophenone-benzhydrol actinometry.[4] For both of the sensitizers employed, $\phi_{t\rightarrow c}/\phi_{isc} \simeq 0.5$,[12] which indicates a reasonable decay ratio ($k_c/k_t \simeq 1$) from the triplet β-tert-butylstyrene to the cis- and trans-isomers, whereas $\phi_{c\rightarrow t}/\phi_{isc}$ is as low as ca. 0.25.[12] This quantum inefficiency in cis-to-trans isomerization would result from a bimolecular decay process through a cis-olefin-sensitizer exciplex.[13]

From these results, it is concluded that the source of the remarkably high ratios of the cis-isomers of β-tert-butylstyrene and β-tert-amylstyrene is mostly attributable to the lower rate constants for the energy transfer from the triplet sensitizers to the cis-isomers than to the trans-isomers.

References and Notes

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2) J. Saltiel, A. Marinari, D. W.-L. Chang, J. C. Mitchener, and E. D. Megarity, J. Am. Chem. Soc., 101, 2982 (1979), and references cited therein.
3) Benzene solutions of olefins (10^{-2} M) were irradiated in the presence of sensitizers (0.5-0.001 M) with a 1 kW high pressure mercury lamp through a Toshiba UVD36B filter for 2-12 hours, during which the photostationary state was performed.
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9) Steric hidrance in cis-β-tert-butylstyrene on the energy transfer process might partly contribute to the decrease in the energy transfer rate.[10]
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11) Irradiation was performed with a 400 W high pressure mercury lamp through a Toshiba UVD36B filter.
12) On derivation of these values the following values were employed; ϕ_{isc}(benzophenone) = 1.0 and ϕ_{isc}(2-acetylnaphthalene) = 0.84 (refs. 4 and 7)
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