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Photosensitized *cis-trans* Isomerization of β-Alkylstyrenes

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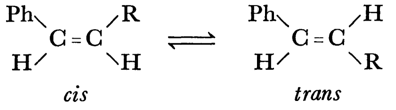
Triplet sensitized isomerization of a series of β-alkylstyrenes has been investigated with the use of various sensitizers. Among the olefins employed β-*t*-butyl- and β-*t*-pentylstyrene were found to give remarkably high ratios of the *cis*-isomers (>80%) at the photostationary state. This fact is reasonably attributed to lower rate constants for energy transfer from the triplet sensitizers to the *cis*-isomers than to the *trans*-isomers.

The mechanism of triplet sensitized *cis-trans* isomerization of aromatic olefins has extensively been investigated.[1,2] However, the isomerization of β-alkylstyrenes has scarcely been learned.[3-8] This paper describes the triplet sensitized isomerization of a series of β-alkylstyrenes, that is, β-methyl- (**1**), β-ethyl- (**2**), β-isopropyl- (**3**), β-*t*-butyl- (**4**), and β-*t*-pentylstyrene (**5**)[9] with the use of triplet sensitizers with different triplet energies. Particularly, it was found that β-*t*-butyl- and β-*t*-pentylstyrenes exhibited remarkably high *cis*-isomer ratios at the photostationary state irrespective of the triplet energies of the sensitizers employed. This fact is reasonably attributed to inefficient energy transfer from the triplet sensitizers to the *cis*-isomers of these olefins as described below.[10]



1: $R=Me$
2: $R=Et$
3: $R=i\text{-}Pr$
4: $R=t\text{-}Bu$
5: $R=t\text{-}C_5H_{11}$

Results and Discussion

Photostationary State Isomer Ratios. Isomeric β-alkylstyrenes, β-methyl-, β-ethyl-, β-isopropyl-, β-*t*-butyl- and β-*t*-pentylstyrene, were irradiated in the presence of sensitizers of various triplet energies in benzene at 26 °C for 2—24 h under degassed conditions with 366-nm light and the resulting photostationary ratios of the *cis*- and *trans*-isomers were accurately determined by GLPC. The pure *cis*- and *trans*-isomers were irradiated in the presence of the sensitizers of higher triplet energies. However, with the sensitizers of lower triplet energies like fluoranthene, benzil, and benz[*a*]anthracene, the irradiation was carried out for mixtures of the *cis*- and *trans*-isomers with compositions close to the photostationary state isomer ratios because of their lower efficiencies for the energy transfer to the olefins. The photostationary state isomer ratios extrapolated to infinite dilution with respect to sensitizer concentration are summarized in Table 1. Figure 1 shows the plots of the photostationary state compositions of these olefins against the triplet energies of the sensitizers employed. As this figure indicates, among the olefins examined, β-methyl-, β-ethyl-, and β-isopropylstyrene show quite similar profiles to that of stilbene[11,12] and confirm a strong similarity in mechanism of the photosensitized isomerization between these three alkylstyrenes and stilbene. On the other hand, β-*t*-butyl- and β-*t*-pentylstyrene exhibit

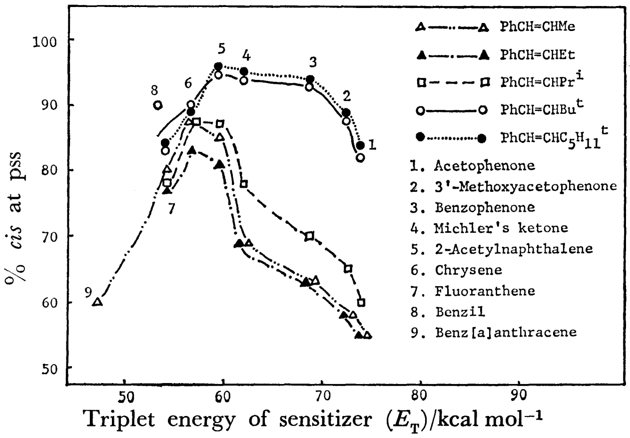


Fig. 1. Photostationary state compositions in triplet sensitized isomerization of β-alkylstyrenes.

Table 1. % *cis* at photostationary state[a)]

Sensitizer	$E_T^{b)}$ kcal mol^{-1}	R in PhCH=CHR				
		Me	Et	*i*-Pr	*t*-Bu	*t*-C_5H_{11}
Acetophenone	73.7	55	55	60	82	84
3′-Methoxyacetophenone	72.4	58	58	65	88	89
Benzophenone	68.6	63	63	70	93	94
Michler's ketone	62	69	69	78	94	95
2-Acetylnaphthalene	59.4	85	81	87	95	96
Chrysene	56.6	88	83	88	90	89
Fluoranthene	54.2	80	77	78	83	84
Benzil	53.4				90	
Benz[*a*]anthracene	47.2	60				

a) In benzene at 26 °C. b) Ref. 13.

quite different profiles from the above olefins; the *cis*-isomer ratios are remarkably high for all sensitizers employed. From the profiles in Fig. 1, the triplet excitation energies of the olefins can be estimated to be *ca.* 62 kcal mol^{-1} for the *cis*-isomers and *ca.* 56 kcal mol^{-1} for the *trans*-isomers of β-methyl-, β-ethyl-, and β-isopropylstyrene, and *ca.* 70 kcal mol^{-1} for the *cis*-isomers and *ca.* 60 kcal mol^{-1} for the *trans*-isomers of β-*t*-butyl- and β-*t*-pentylstyrene according to the well known method.[12]

The present photosensitized isomerization is assumed, by analogy with the isomerization of stilbene,[11] to proceed simply through the following processes,

$$\mathrm{S} \xrightarrow{h\nu} {}^1\mathrm{S}^* \xrightarrow{\Phi_{\mathrm{isc}}} {}^3\mathrm{S}^* \tag{1}$$

$${}^3\mathrm{S}^* \longrightarrow \mathrm{S} \tag{2}$$

$${}^3\mathrm{S}^* + \mathrm{t} \xrightarrow{k_{\mathrm{st}}} \mathrm{S} + {}^3\mathrm{t}^* \tag{3}$$

$${}^3\mathrm{S}^* + \mathrm{c} \xrightarrow{k_{\mathrm{sc}}} \mathrm{S} + {}^3\mathrm{c}^* \tag{4}$$

$${}^3\mathrm{c}^* \longrightarrow {}^3\mathrm{p}^* \tag{5}$$

$${}^3\mathrm{t}^* \longrightarrow {}^3\mathrm{p}^* \tag{6}$$

$${}^3\mathrm{p}^* \xrightarrow{k_{\mathrm{d}}} \alpha\mathrm{t} + (1-\alpha)\mathrm{c}, \tag{7}$$

where S stands for a sensitizer, t, c, and p mean transoid, cisoid, and twisted species, respectively, and α is the decay ratio from the twisted triplets to the *trans*-isomers of the olefins.

Based on the above scheme, the photostationary state composition, $([\mathrm{t}]/[\mathrm{c}])_{\mathrm{pss}}$, is expressed by Eq. 8 and the quantum yields of *trans*-to-*cis* and *cis*-to-*trans* isomerization, $\Phi_{\mathrm{t}\to\mathrm{c}}$ and $\Phi_{\mathrm{c}\to\mathrm{t}}$, by Eqs. 9 and 10, respectively.

$$([\mathrm{t}]/[\mathrm{c}])_{\mathrm{pss}} = \frac{k_{\mathrm{sc}}}{k_{\mathrm{st}}}\frac{\alpha}{1-\alpha} \tag{8}$$

$$\Phi_{\mathrm{t}\to\mathrm{c}} = \Phi_{\mathrm{isc}}(1-\alpha) \tag{9}$$

$$\Phi_{\mathrm{c}\to\mathrm{t}} = \Phi_{\mathrm{isc}}\alpha \tag{10}$$

Equation 8 suggests that the observed high ratios of the *cis*-isomers at the photostationary state of the β-*t*-alkylstyrenes might originate from the following possibilities: (1) The triplet state sensitizer, ${}^3\mathrm{S}^*$, would undergo faster excitation transfer to the *trans*-isomers than to the *cis*-isomers ($k_{\mathrm{st}} > k_{\mathrm{sc}}$), and/or (2) the twisted triplet states, ${}^3\mathrm{p}^*$, of the olefins would decay more efficiently to the *cis*-isomer than to the *trans*-isomer ($1-\alpha > \alpha$). In order to examine these possibilities attempts were made to determine the rate constants for the energy transfer and the quantum yields for the isomerization.

Rate Constants for Energy Transfer. Determination of the rate constants for triplet excitation transfer to the representative olefins, *cis*- and *trans*-β-methylstyrenes, and β-*t*-butylstyrenes, was undertaken for typical triplet sensitizers, benzophenone and chrysene, at ambient temperature. The rate constants for quenching of phosphorescence of benzophenone with these olefins were measured in carbon tetrachloride with the single photon counting technique, and quenching rate of the triplet-triplet absorption of chrysene with the olefins were determined in cyclohexane by the flash photolysis technique. The measured rate constants are summarized in Table 2.

TABLE 2. RATE CONSTANTS FOR QUENCHING OF EXCITED TRIPLET SENSITIZERS BY β-ALKYLSTYRENES IN BENZENE[a)]

Sensitizer	Olefin	$k_{\mathrm{st}}/\mathrm{l\ mol^{-1}\ s^{-1}}$	$k_{\mathrm{sc}}/\mathrm{l\ mol^{-1}\ s^{-1}}$
Chrysene	PhCH=CHMe	5.4×10^{7}	8.8×10^{6}
	PhCH=CHBu^t	1.1×10^{7}	6.2×10^{5}
Benzophenone	PhCH=CHMe	1.95×10^{9}	1.21×10^{9}
	PhCH=CHBu^t	1.21×10^{9}	1.25×10^{8}

a) At ambient temperature.

As Table 2 indicates, in the case of β-methylstyrenes, triplet benzophenone (E_{T}=68.6 kcal mol^{-1})[13] transfers excitation energy to both *cis*- and *trans*-isomers with nearly diffusion-controlled rate constants, but slightly less efficiently to the *cis*-isomer; however, the excitation transfer from triplet chrysene (E_{T}=56.6 kcal mol^{-1})[13] is much slower than the diffusion-controlled rate and the rate constant for the *cis*-isomer is six times smaller than to the *trans*-isomer. As for the excitation transfer to β-*t*-butylstyrenes, even when benzophenone was used as a sensitizer, the rate constant for the *cis*-isomer is about ten times lower than that for the *trans*-isomer. The magnitude of the rate constants is in good agreement with the aforementioned estimate of the triplet excitation energies of the olefins and suggests that the remarkably high composition of the *cis*-isomer of the β-*t*-alkylstyrenes at the photostationary state is mostly due to the smaller energy transfer rate constants from the triplet sensitizers to the *cis*-isomers.

Furthermore, the results in Table 2 indicate that the rate constants of the energy transfer are governed not only by the *exo*- and *endo*-thermicity of the processes but also by the steric effects exerted from the crowded olefins on approach to the triplet sensitizers. Thus, triplet benzophenone undergoes energy transfer to *cis*-β-methylstyrene about 1.6 times more slowly than to its *trans*-isomer. From the results of photoelectron spectroscopy, *cis*-β-methylstyrene is presumed to take a conformation where its benzene ring is twisted about 20° from the C=C molecular plane.[14] Therefore, the slower rate of energy transfer to the *cis*-isomer might be caused by the steric effect exerted by its twisted conformation to prevent the approach of the triplet sensitizer.[15] Also, the energy transfer rate from triplet benzophenone to *trans*-β-*t*-butylstyrene is about 1.6 times lower than to *trans*-β-methylstyrene. *trans*-β-*t*-Butylstyrene takes a planar conformation similar to that of *trans*-β-methylstyrene.[14] Accordingly, the triplet excitation energy of *trans*-β-*t*-butylstyrene will be close to that of *trans*-β-methylstyrene, 59.8 kcal mol^{-1} as reported by Lamola and Hammond[8] or less as suggested by the profile in Fig. 1. These results clearly indicate that in the energy transfer from triplet benzophenone the presence of the bulky *t*-butyl group in β-*t*-butylstyrene exerts steric hindrance to reduce the rate for accepting triplet energy as compared to the case of *trans*-β-methylstyrene. Herkstroeter, Jones, and Hammond showed the steric effect exerted in energy transfer from triplet states of sterically hindered benzophenones to stilbene.[16] The

Table 3. Quantum yield of isomerization of β-*t*-butylstyrene[a)]

Sensitizer	Sensitizer concn mol l⁻¹	Olefin concn mol l⁻¹	$\Phi_{t\to c}/\Phi_{isc}$	$\Phi_{c\to t}/\Phi_{isc}$
Benzophenone	0.1	0.02	0.53	0.23
	0.1	0.05	0.55	0.25
2-Acetyl-naphthalene	0.35	0.02	0.48	0.094
	0.35	0.05	0.49	0.15
		∞		0.24[b)]

a) In benzene at 26 °C. b) Quantum yield extrapolated to infinite olefin concentration.

present results provide an example of steric effects brought about by triplet energy acceptors on the energy transfer process.

The energy transfer rate from triplet benzophenone to *cis*-β-*t*-butylstyrene is about ten times lower than that to *trans*-β-*t*-butylstyrene. *cis*-β-*t*-Butylstyrene is presumed by PES to take a conformation where its benzene ring is twisted about 70° from the C=C molecular plane.[14)] The highly twisted conformation will increase its triplet excitation energy to make the energy transfer from triplet benzophenone endothermic and will sterically hinder the approach of the triplet sensitizer.

Quantum Yields. Table 3 summarizes typical results of the quantum yields for the isomerization of β-*t*-butylstyrenes using benzophenone and 2-acetylnaphthalene as sensitizers. Both sensitizers give nearly the same value, 0.5±0.05, for $\Phi_{t\to c}/\Phi_{isc}$, which means that the energy transfer effectively takes place from the triplets of both sensitizers to the *trans*-isomer. The above value is in good agreement with the results of β-methylstyrene with various sensitizers reported by Caldwell.[3)] The value for $\Phi_{c\to t}/\Phi_{isc}$ is nearly 0.25 in benzophenone sensitization almost irrespective of the olefin concentration. However, in 2-acetylnaphthalene sensitization, the value tends to increase with the olefin concentration, and leads to 0.24 by extrapolation to infinite olefin concentration, which agrees well with the above value for benzophenone sensitization. However, the value for $\Phi_{c\to t}/\Phi_{isc}$ thus obtained remains still nearly half of $\Phi_{t\to c}/\Phi_{isc}$.

This quantum inefficiency in the *cis*-to-*trans* process would result from formation of a *cis*-olefin-sensitizer exciplex followed by its decay to the *cis*-olefin as suggested by Caldwell[3,17)] in the sensitized isomerization of β-methylstyrene with low energy sensitizers.

Effects of Sensitizer Concentration, Azulene, and Oxygen. Quenching of excited states with a number of species including ground-state sensitizers, azulene, and oxygen can serve to explore triplet energy surfaces of olefins as investigated on stilbene.[18,19)]

These processes are expressed by Eqs. 11—14, where Az stands for azulene.

$$^3t^* + S \xrightarrow{k_{ts}} t + {}^3S^* \tag{11}$$

$$^3t^* + Az \xrightarrow{k_{az}} t + {}^3Az^* \tag{12}$$

$$^3t^* + O_2 \xrightarrow{k_{ot}} t + O_2 \tag{13}$$

$$^3p^* + O_2 \xrightarrow{k_{op}} \alpha t + (1-\alpha)c + O_2 \tag{14}$$

The quenching of the *trans* triplet, $^3t^*$, by azulene might be an energy transfer process, and the quenching of $^3t^*$ by oxygen, if it takes place, should be energy transfer, but the quenching of the twisted triplet, $^3p^*$, by oxygen might be enhancement of the intersystem crossing from $^3p^*$ to a ground state with twisted geometry and this quenching cannot affect the photostationary state isomer ratios. Reactions 11, 12, and 14 were inferred to occur actually for stilbene.[18,19)]

In the present investigation, attempts were done to examine the effects of azulene, oxygen, and sensitizer concentration on the photostationary isomer ratios in benzophenone-sensitized isomerization of β-methyl- and β-*t*-butylstyrene. However, no measurable effect was observed. This fact agrees with a previous result that azulene did not affect the photostationary isomer ratios in benzophenone-sensitized isomerization of β-methylstyrene.[20)] The above results for the β-alkylstyrenes are in contrast with the results of stilbene, for which azulene and the sensitizer concentration are effective to change the photostationary isomer ratio.[18)] Therefore, for β-alkylstyrenes, Reactions 11, 12, and 13 are unimportant, although Reaction 14 might be operative. The present results suggest that the *trans* as well as *cis* triplets of the β-alkylstyrenes are alive in too short lifetimes to be quenched by azulene, sensitizer, or oxygen, and undergo rapid relaxation into the twisted triplets which are incapable of being quenched by azulene. This mechanism is in contrast with the *trans* triplets of stilbene.[18)]

Experimental

The NMR spectra and UV spectra were recorded on a JEOL JNM-MH-100 spectrometer and a Hitachi 200-20 spectrophotometer, respectively. Gas-liquid chromatographic analysis was performed on a Shimadzu GC-4CM-PF gas chromatograph equipped with an FID and a Hitachi K53 gas chromatograph equipped with a TCD was used for preparative purposes.

Materials. Isomeric β-methyl- (**1**), β-ethyl- (**2**), and β-*t*-butylstyrenes (**4**), were prepared as described previously.[13)] A mixture of *cis*- and *trans*-β-isopropylstyrene (**3**) was prepared from 2-methylpropanal and benzyltriphenylphosphonium bromide according to literature.[21)] Pure *cis*- and *trans*-**3** were separated by GLPC (polyethylene glycol 20 M (10%)). A mixture of *cis*- and *trans*-β-*t*-pentylstyrene (**5**) was similarly prepared. Pure *cis*- and *trans*-**5** were separated by column chromatography. Their structures were identified by NMR spectroscopy. The purity of all the samples was more than 99% as determined by GLPC (polyethylene glycol 20 M (5%)). These olefins were distilled under reduced pressure before use.

cis-**5**, bp 80—82 °C/12 Torr (1 Torr=133.322 Pa); NMR (CCl_4): δ 0.82 (t, *J*=6.0 Hz, 3H, C=C-C-C-CH_3), 0.88 (s, 6H, C=C-C(CH_3)$_2$-), 1.31 (q, *J*=6.0 Hz, 2H, C=C-C-CH_2-), 5.40 (d, *J*=12.6 Hz, 1H, Ph-C=CH-), 6.40 (d, *J*=12.6 Hz, 1H, PhCH=C-), 7.09 (m, 5H, aromatic H); Found: C, 89.73; H, 10.50%. Calcd for $C_{13}H_{18}$: C, 89.58; H, 10.41%.

trans-**5**, bp 84—86 °C/12 Torr; NMR (CCl_4): δ 0.85 (t, *J*=7.0 Hz, 3H, C=C-C-C-CH_3), 1.07 (s, 6H, C=C-C(CH_3)$_2$-), 1.51 (q, *J*=7.0 Hz, 2H, C=C-C-CH_2-), 6.08 (d, *J*=16.0 Hz, 1H, PhC=CH–), 6.23 (d, *J*=16.0 Hz, 1H, Ph–CH=C–), 7.25 (m, 5H, aromatic H). Found: C, 89.54; H, 10.49%. Calcd for $C_{13}H_{18}$: C, 89.58; H, 10.41%.

Benzene was purified by distillation. Aromatic hydrocarbons used as sensitizers were purified by column chromatography and recrystallization. Acetophenone and 3′-methoxyacetophenone were purified by distillation. Other aromatic ketones were purified by recrystallization.

Determination of the Photostationary State Isomer Ratios on Irradiation of 366-nm Light. Benzene solutions (3 ml) of a desired concentration of a sensitizer and *cis*- and *trans*-β-alkylstyrenes in Pyrex tubes were degassed using freeze-thaw cycles under about 10^{-5} Torr, and irradiated for 2—24 h by a 1 kW high pressure mercury lamp immersed in a Pyrex cooling well and further surrounded by Toshiba UV-D36B glass filters using a merry-go-round type Riko RH400-10W rotary photochemical reactor. The glass filters were used for isolation of the 366-nm line. The isomer ratios of *cis*- and *trans*-β-alkylstyrenes were determined by GLPC analysis. The following columns were used for quantitative analysis: polyethylene glycol 20 M (5%), Thermon 1000 (5%), and Silicone XF-1150 (5%).

Quantum Yield Measurements Using 366-nm Light. Benzene solutions of either a pure *cis* or *trans* substrate and a sensitizer in Pyrex tubes were degassed by freeze-thaw cycles and were irradiated in parallel with a 400 W high pressure mercury lamp surrounded by Toshiba UV-D36B glass filters using a merry-go-round type reactor. Light intensity was determined by benzophenone-benzhydrol actinometry using the method of Moore and Ketchum.[21] After being irradiated for 10 min the tubes containing the actinometry solutions were opened, and the contents were diluted with benzene and analyzed by UV spectroscopy. The total period of irradiation was adjusted so that usually 2—8% of an isomer was converted and the conversion was determined quantitatively by GLPC analysis.

Measurements of Photostationary State Isomer Ratios in the Presence of Azulene and/or Oxygen. Benzene solutions containing benzophenone (0.1 mol l^{-1}) and a *cis*- or *trans*-β-alkylstyrene and varying amounts of azulene (0.01—0.03 mol l^{-1}) in Pyrex tubes were degassed, aerated, or saturated with oxygen and irradiated for 2 h by a 1 kW high pressure mercury lamp surrounded by Toshiba UV-D36B glass filters using a merry-go-round type reactor. The isomer ratios of *cis*- and *trans*-β-alkylstyrenes were determined by GLPC analysis.

Rate Constants for Energy Transfer from Triplet Benzophenone to β-Alkylstyrenes. Phosphorescence lifetimes of benzophenone (1.1×10^{-3} mol l^{-1}) were measured in carbon tetrachloride at ambient temperature using a single photon counting apparatus, an Applied Photophysics SP-3X system, in the absence and in the presence of varying concentrations of *cis*- and *trans*-β-methyl- and β-*t*-butylstyrenes. The solutions were deaerated by bubbling with argon for more than 30 min. The phosphorescence lifetime of benzophenone monitored at 452 nm in this solvent in the absence of quenchers was 23 μs and the lifetime was diminished by addition of the quenchers. The energy transfer rate constants were calculated from these experiments.

Rate Constants for Energy Transfer from Triplet Chrysene to β-Alkylstyrenes. Rate constants for energy transfer from triplet chrysene to *cis*- and *trans*-β-methyl- and β-*t*-butylstyrenes were obtained by the measurements of lifetimes of the triplet-triplet absorption of chrysene monitored at 570 nm on a conventional flash photolysis apparatus (Applied Photophysics).

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9) In the present paper trivial names are used instead of systematic names, because the former is thought to help the readers in their better understanding of the contents. The systematic names are as follows: **1**, 1-phenyl-1-propene; **2**, 1-phenyl-1-butene; **3**, 3-methyl-1-phenyl-1-butene; **4**, 3,3-dimethyl-1-phenyl-1-butene; **5**, 3,3-dimethyl-1-phenyl-1-pentene.

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