Secondary Deuterium Isotope Effects on the Transfer of Triplet Excitation

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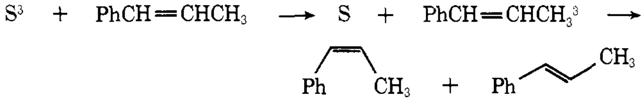
Abstract: Secondary deuterium isotope effects are shown to be a useful mechanistic tool in the study of triplet excited state reactions. The cis–trans isomerization of β-methylstyrene photosensitized by various sensitizers is shown to involve transfer of triplet excitation. Isotope effects on the reaction are significant; they depend on the position of deuterium and to some extent on the geometry of the olefin. The results indicate vertical excitation transfer to the trans isomer and imply nonvertical excitation transfer to the cis isomer, invariant to the type of sensitizer in the triplet energy range of 53–57 kcal/mol. The implications of these results for photochemical mechanistic studies are discussed. A tentative model for olefin–sensitizer interaction in nonvertical excitation transfer is presented.

In the last 15 years or so, secondary deuterium kinetic isotope effects have been observed in numerous reactions.[1] There are several possible origins of these isotope effects,[1] and in some cases opinions differ as to their origin.[2] Nevertheless, these isotope effects have proved very useful in probing the bonding and geometry of transition states. For example, the single most cogent experiment requiring a concerted mechanism for the Diels–Alder reaction involves secondary deuterium isotope effects.[3]

It has been our hope to extend secondary deuterium isotope effect studies to excited state reactions in a systematic fashion. We have begun these studies[4,5] with an examination of the triplet excitation transfer process, since several interesting questions arise in connection with it. (1) Are triplet biradicals involved as intermediates? (2) Is the donor–acceptor interaction fundamentally dependent on the chemical nature of either partner? (3) What are the geometries of the partners, either at the moment of excitation transfer or in a weakly bound exciplex intermediate? We have studied the interaction of various sensitizers with specifically labeled β-methylstyrene as a model system.



$$S^3 + PhCH{=}CHCH_3 \longrightarrow S + PhCH{=}CHCH_3{}^3 \longrightarrow$$

Experimental Section

Materials. Benzophenone, 2-acetonaphthone, and fluorenone were twice recrystallized from hexane and sublimed. Thioxanthone and chrysene were twice recrystallized from toluene; thioxanthone was sublimed. Biacetyl was distilled through a 1-ft Vigreux column at atmospheric pressure under nitrogen. Dodecane, used as internal standard, was purified as previously described.[6]

Benzene solvent was shaken four times with cold concentrated sulfuric acid, rinsed with distilled water, dried over anhydrous magnesium sulfate, and distilled from phosphorus pentoxide. Final purification was achieved by two successive fractional freezings, in each of which approximately half the material was retained.

Deuterated β-Methylstyrenes. (1) β-Deuterated. (a) Ethyltriphenylphosphonium bromide was labeled at the α position of the ethyl group[7] by metalation with phenyllithium followed by quenching with D_2O. A repeat of this procedure following reisolation of the phosphonium salt afforded material of *ca.* 64% deuteration of the two methylene hydrogens. Formation of the ylide and addition of freshly distilled benzaldehyde in dry dimethoxyethane afforded a mixture of *cis-* and *trans-β*-methylstyrene-*β-d* of 84% isotopic purity (by low-voltage mass spectrometry; *vide infra*). Separation of the isomers from solvent and from one another was accomplished by distillation on a spinning band column followed by preparative vpc (*vide infra*).

(b) Reflux of 30 g of propiophenone with 10 g of D_2O and 5 g of triethylamine afforded (after reflux for 2 hr, partition between hexane and 10% hydrochloric acid, water washing, and solvent removal) 25 g of propiophenone labeled (nmr) with 55% of two deuteriums at the methylene position. Treatment of the deuterated ketone with 3 g of sodium borohydride in cold methanol afforded (after standing briefly to partition between water and hexane, and solvent evaporation of the dry hexane layer) crude 1-phenyl-1-propanol. Dehydration of the crude alcohol in 30 ml of 85% phosphoric acid afforded, after distillation, a mixture of β-methylstyrenes (17 g) in which trans predominated; nmr analysis indicated *ca.* 60% deuteration. This material gave isotope effects identical with those obtained with material prepared by the Wittig route (in which the position of deuteration is unambiguous).

(2) The α-deuterio compound was prepared by the Wittig reaction sequence utilizing unlabeled ethyltriphenylphosphonium bromide and benzaldehyde-*α-d* prepared by the method of Olofson and Zimmerman.[8] Low-voltage mass spectrometry indicated 68 ± 1% monodeuterated olefin; nmr indicated 71 ± 2%.

(3) *p*-Deuterio Compound. A similar Wittig reaction with 4-bromobenzaldehyde[9] afforded a cis–trans mixture of *p*-bromo-β-methylstyrene, which was converted to the *p*-deuterio compound *via* formation of the Grignard reagent in dry ether followed by quenching with D_2O. After preparative vpc, 75% monodeuteration was determined for the β-methylstyrene by mass spectral analysis.

(4) The *m*-deuterio compound was prepared as follows. Grignard addition of 3-bromobenzaldehyde[9] (7.5 g) and excess ethylmagnesium bromide, followed by dehydration of the crude carbinol in hot 86% phosphoric acid (105° for 90 min), afforded 3-bromo-β-methylstyrene, bp 92–94° (0.3 mm), yield 5.8 g (64%). The Grignard reagent of this bromo compound was quenched with 2 g of D_2O. Distillation afforded 1.5 g (40%) of a mixture of *cis-* and *trans-β*-methylstyrene-*m-d* analyzing mass spectrometrically at 80% deuteration. Further purification was effected by preparative vpc.

All deuterated β-methylstyrenes could be separated into cis and trans isomers *via* preparative vpc ($^3/_8$ in. × 6 ft Carbowax 20M

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(1) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1, 109 (1963).

(2) E. R. Thorton, *Annu. Rev. Phys. Chem.*, 17, 349 (1966).

(3) S. Seltzer, *J. Amer. Chem. Soc.*, 87, 1534 (1965).

(4) R. A. Caldwell and G. W. Sovocool, *ibid.*, 90, 7138 (1968).

(5) R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *ibid.*, 93, 779 (1971).

(6) R. A. Caldwell, *J. Org. Chem.*, 34, 1889 (1968).

(7) M. Schlosser, *Chem. Ber.*, 97, 3219 (1964).

(8) R. A. Olofson and D. M. Zimmerman, *J. Amer. Chem. Soc.*, 89, 5057 (1967).

(9) Aldrich Chemical Co. Oxidation afforded the corresponding bromobenzoic acid; the ultimate position of the label is thus unquestionable.

column, 100–120°). It was routinely possible, by rechromatographing the isolated material, to obtain gram quantities of either cis or trans isomers in which <0.1% isomeric contamination and <0.5% total impurity (by vpc) remained. For isolation of the cis isomer, it was generally convenient to induce photosensitized isomerization with 2-acetonaphthone or chrysene (overnight exposure to a Hanovia 450-W medium-pressure lamp, hexane solvent, Pyrex or Corning 3320 filter sleeve) prior to vpc separation.

The nmr spectra of all deuterated products were consistent with the structures required by the method of synthesis. Each compound was diluted after purification with unlabeled β-methylstyrene to give rise roughly to 40–50% deuterium content and analyzed mass spectrometrically at low voltage after one further vpc collection.

Mass spectrometric deuterium analyses were done at 6.5–8.0 V ionizing voltage on a consolidated Model 21-103 mass spectrometer. The conditions ensured that loss of one hydrogen to give P − 1 peaks was held to 1–2% or less. Ratios of unlabeled to labeled material (H/D) were calculated (from the average of 6–20 scans of the *m/e* 117–120 region) as H/D = *m/e* 118 signal/(*m/e* 119 signal − 0.0989 *m/e* 118 signal), thus correcting $^{12}C_9H_9D$ for its $^{12}C_8{}^{13}C_1H_{10}$ contribution. Reproducibility was measured from the 90% confidence level of the mean of a consecutive series of repetitive scans, the average deviation from the mean within that same series, and by comparison of the mean values obtained for the identical sample on different days. By all three criteria, the precision of the H/D ratio was typically ±0.01–±0.015, giving rise to ±0.015–±0.02 uncertainty in the isotope effects.

Isotope effects were determined in benzene, with sensitizer concentration adjusted so that absorbance at 3660 Å (Corning 7-83 Filter) was *ca.* 2–4. The irradiations of thrice outgassed and sealed 13-mm ampoules of sensitizer and 0.1–0.5 *M* β-methylstyrene were performed in a "merry-go-round" apparatus, either in a rotating mode when precise (±2%) actinometry was required or in a stationary mode, with inserts designed to provide reproducible positioning of the ampoules closer to the source, when less precise (±5–10%) actinometry was acceptable as the price of the higher light flux thereby achieved. After irradiation until isomerization yields ranged from 2 to 17% (but never more than 20% of the way to photostationary state), the samples were analyzed by vpc for precise conversion, concentrated in a slow stream of argon, and subjected to preparative vpc. Appropriate controls established that neither the vpc collection process nor the evaporation caused any change in the apparent H/D ratio. From the H/D ratios in starting material and product, the isotope effects could be calculated; *cf.* eq 11.

In some cases, irradiation to photostationary state was performed; vpc collection in these cases could be performed similarly.

The results presented herein relate to "selected" data. In our hands, and particularly in the initial phases of each man's work, several systematic errors appeared. They could be traced to a variety of causes: (1) incomplete vpc separation; (2) incomplete evacuation of the previous sample from the gas inlet system of the mass spectrometer prior to admission of the next one; (3) retention of prior sample in stopcock grease. All results presented here reflect those experiments in which these problems were known to be absent.

Quantum yields were measured *via* potassium ferrioxlate actinometry. The merry-go-round apparatus was utilized. Nominal 3.2-ml samples of sensitizer, nominally 0.05 *M* in β-methylstyrene, were irradiated until *ca.* 3–10% isomerization had occurred. Each ampoule contained dodecane as internal standard to check for material balance. Standard mixtures of cis, trans, and dodecane were injected each time a batch of quantum yields was measured in order to check relative detector sensitivities.

Photostationary states were performed by irradiation of ampoules until the cis:trans ratio was identical (±1%) for samples starting with cis and trans. For all sensitizers but biacetyl, material balance (referenced to dodecane internal standard) was *ca.* 95% or better at photostationary state. A slow disappearance of β-methylstyrene ($\phi \sim 0.03$) on prolonged irradiation with biacetyl was observed.

Results

Triplet Excitation Transfer. The kinetics of triplet excitation transfer in this system follow directly from the work of Hammond, *et al.*,[10,11] on the closely related stilbenes. We intend to draw extensive inferences from kinetic data, and from the close analogy of our kinetic results with those for stilbene and α-methylstilbene. We present at this point a kinetic framework which will allow us to demonstrate by analogy with the stilbenes that triplet excitation transfer is indeed the mechanism for photosensitized isomerization of the β-methylstyrenes. It will be extended in a later section to describe the isotope effect experiments. In eq 1–6, *t*-H and *c*-H stand for unlabeled *trans*- and *cis*-β-methylstyrene and S stands for a sensitizer with intersystem crossing quantum yield ϕ_{isc}.

$$\mathrm{S} \xrightarrow{h\nu} \mathrm{S}^1 \xrightarrow{\phi_{\text{isc}}} \mathrm{S}^3 \tag{1}$$

$$\mathrm{S}^3 \xrightarrow{k_{\text{sD}}} \mathrm{S} \tag{2}$$

$$\mathrm{S}^3 + t\text{-H} \xrightarrow{k_{\text{s}t\text{-H}}} \mathrm{S} + \mathrm{H}^3 \tag{3H}$$

$$\mathrm{S}^3 + c\text{-H} \xrightarrow{k_{\text{s}c\text{-H}}} \mathrm{S} + \mathrm{H}^3 \tag{4H}$$

$$\mathrm{H}^3 \xrightarrow{k_{t\text{-H}}} t\text{-H} \tag{5H}$$

$$\mathrm{H}^3 \xrightarrow{k_{c\text{-H}}} c\text{-H} \tag{6H}$$

If eq 2 is entirely suppressed by eq 3 or 4

$$\phi_{t\text{-H}\rightarrow c\text{-H}} = \phi_{\text{isc}}k_{c\text{-H}}/(k_{c\text{-H}} + k_{t\text{-H}}) \equiv \phi_{\text{isc}}\alpha_{\text{H}} \tag{7a}$$

$$\phi_{c\text{-H}\rightarrow t\text{-H}} = \phi_{\text{isc}}k_{t\text{-H}}/(k_{c\text{-H}} + k_{t\text{-H}}) \equiv \phi_{\text{isc}}(1 - \alpha_{\text{H}}) \tag{7b}$$

The independent determination[12,13] of ϕ_{isc} allows determination of α_{H}. We find $\alpha_{\text{H}} = 0.50 \pm 0.03$, independent of sensitizer, from $\phi_{t\text{-H}\rightarrow c\text{-H}}$ studies (*cf.* Table I). If decay from an olefin–sensitizer exciplex[13] were important in the present case, the apparent α_{H} values would be lower than the true one and should be sensitizer-dependent. Since $\alpha_{\text{H}} = 0.50$ is quite reasonable for an olefin triplet,[10] and since the data in Table I for the two high-energy sensitizers survive the check that $\alpha_{\text{H}} + (1 - \alpha_{\text{H}}) \equiv 1$, the data rule out such bimolecular decay in the trans case for all sensitizers. For fluorenone and biacetyl with *cis*-β-methylstyrene, exciplex decay is not ruled out. However, $k_{\text{s}c\text{-H}}$ is surely small; if k_{sD} (eq 2) enters significantly, these two quantum yields

Table I. Quantum Yields for Sensitized β-Methylstyrene Isomerization[a]

ϕ_{isc}	Sensitizer (E_T, kcal/mol)[b]	$\phi_{t\rightarrow c}/\phi_{\text{isc}} \equiv \alpha_{\text{H}}$	$\phi_{c\rightarrow t}/\phi_{\text{isc}} \equiv 1 - \alpha_{\text{H}}$
1.00[c]	Propiophenone (74.6)	0.51	0.50
1.00[c]	Benzophenone (68.5)	0.51[c]	0.51[c]
0.67[c]	Chrysene (56.6)	0.48[f]	
0.99[b]	Biacetyl (54.9)	0.50[d,e]	0.30[d,e]
0.93[c]	Fluorenone (53.3)	0.53[d]	0.33[d]

[a] All experiments performed with 0.05 *M* olefin at 3660 Å unless otherwise noted. Precision of these numbers is +0.03. [b] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298. [c] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43** 2129 (1965). [d] Extrapolated to infinite olefin concentration by a two-point $1/\phi$ *vs.* 1/concentration plot (0.05 and 0.5 *M*). The $\phi_{c\rightarrow t}$ values showed only slight sensitivity to concentration. The $\phi_{c\rightarrow t}$ values were quite sensitive to concentration and may well be seriously in error. [e] 4360 Å. [f] 0.14–0.24 *M*.

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[10] G. W. Hammond, *et al.*, *J. Amer. Chem. Soc.*, 86, 3197 (1964).

[11] W. G. Herkstroeter and G. S. Hammond, *ibid.*, 88, 4769 (1966).

[12] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965); however, *cf.* ref 13.

[13] R. A. Caldwell and R. P. Gajewski, *J. Amer. Chem. Soc.*, 93, 532 (1971).

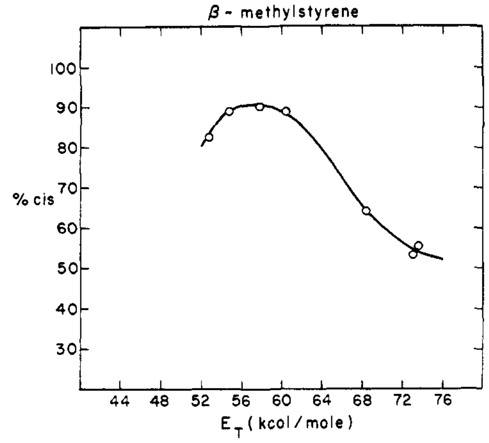

Figure 1. Photostationary state composition of β-methylstyrene in the presence of the various sensitizers.

would also be attenuated. No decision as to the origin of the inefficiency is possible.

$$\left.\frac{(c\text{-H})}{(t\text{-H})}\right|_{\text{PSS}} = \frac{k_{st\text{-H}}\,k_{c\text{-H}}}{k_{sc\text{-H}}\,k_{t\text{-H}}} \tag{8H}$$

Examination of photostationary state composition as a function of sensitizer triplet excitation energy in terms of eq 8 (the "Saltiel plot"[10]) confirms a strong similarity in mechanism between photosensitized β-methylstyrene and stilbene isomerizations. Equation 8 and its inherent assumptions have been discussed at length for the stilbenes.[10,11] Our data (Table II and Figure 1) bear a striking resemblance to the stilbene and α-methylstilbene data, though a shift in the entire Saltiel plot to higher sensitizer energy occurs. The shift is entirely expected, since the olefin triplet excitation energy is higher: *cf. trans*-stilbene (50 kcal/mol[10]) and *trans*-β-methylstyrene (59.8[12]). Our data suggest *ca.* 70 kcal/mol for *cis*-β-methylstyrene, *cf.* 57 kcal/mol[10] for *cis*-stilbene.

Table II. Photostationary States (PSS) in Sensitized β-Methylstyrene Isomerization

Sensitizer, E_T	c-H/t-H$\vert_{\text{PSS}}$	% cis at PSS[a]
Propiophenone (74.6)	1.22	55.1
Xanthone (74.2)	1.07	51.8
Benzophenone (68.5)	1.79	64.2
2-Acetonaphthone (59.3)	6.60	86.9
α-Naphthyl phenyl ketone (57)	7.1	87.7
Chrysene (56.6)	~7[b]	~87.5[b]
Biacetyl (54.9)	7.7 ± 0.3	88.5 ± 0.2
Fluorenone (53.3)	5.0 ± 0.05	83.3 ± 0.01

[a] Except as noted, error is ±5% in the cis–trans ratio. [b] Approached from trans side only; the value given is thus a lower bound.

Rate contents for excitation transfer from fluorenone and biacetyl to *trans*-β-methylstyrene have been measured, by irradiation at 436 nm, utilizing anthracene (E_T = 42 kcal/mol[14]) as a diffusion-controlled quencher (k_q assumed as $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$). The measured rate constants, $k_{st\text{-H}} = 1.1 \pm 0.2 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ for fluorenone and $8 \pm 2 \times 10^6\ M^{-1}\ \text{sec}^{-1}$ for biacetyl, indicate processes substantially slower than diffusion-controlled. These two energy transfer reactions, based on spectroscopic triplet energies, are 6.5 and 5 kcal/mol endothermic, respectively. These rate constants compare closely with data for excitation transfer of comparable endothermicity from sensitizers to *trans*-stilbene, a vertical[11] acceptor. The comparison is also adequate with vertical excitation–transfer rate constants involving sensitization and quenching of biacetyl phosphorescence.[14,15] We interpret these comparisons to mean that *trans*-β-methylstyrene is probably also a vertical acceptor.

We conclude that an adequate basis exists, without recourse to isotope effects, for concluding that photosensitized β-methylstyrene isomerization occurs with much the same detailed mechanism as stilbene.

Table III. Isotope Effects[a] on the Isomerization of *trans*-β-Methylstyrene to *cis*-β-Methylstyrene

	Position of monodeuteration			
Sensitizer (E_T, kcal/mol)	β	α	*p*	*m*
Propiophenone (74.6)	1.00	0.99		
Benzophenone (68.5)	0.98			
2-Acetonaphthone (59.3)	1.13			
Chrysene (56.6)	1.13	1.05	1.04	
Biacetyl (54.9)	1.14	1.05	1.05	1.01
Fluorenone (53.3)	1.15	1.08	1.06	1.02

[a] Values given are $(k_{st\text{-H}}/k_{st\text{-D}})(\alpha_H/\alpha_D)$ as determined by the method of eq 11. Precision is judged to be ±0.015 to ±0.02 as judged by reproducibility of the mass spectral analysis or by the agreement between replicate experiments.

Isotope Effect Experiments. Table III shows the results obtained for trans to *cis* isomerization of β-methylstyrene. The addition of the following equations to eq 1–8 permits kinetic analysis; here D signifies a specifically deuterated β-methylstyrene.

$$\text{S}^3 + t\text{-D} \xrightarrow{k_{st-\text{D}}} \text{S} + \text{D}^3 \tag{3D}$$

$$\text{S}^3 + c\text{-D} \xrightarrow{k_{sc-\text{D}}} \text{S} + \text{D}^3 \tag{4D}$$

$$\text{D}^3 \xrightarrow{k_{t-\text{D}}} t\text{-D} \tag{5D}$$

$$\text{D}^3 \xrightarrow{k_{c-\text{D}}} c\text{-D} \tag{6D}$$

From the kinetic scheme, the initial quantum yields of *c*-H and *c*-D obtained in excitation transfer to a mixture of *t*-H and *t*-D are given, respectively, by eq 9 and 10; α_D is defined for deuterated olefin analogously to eq 7a for α_H.

$$\phi_{c\text{-H}} = \phi_{\text{isc}} \frac{k_{st\text{-H}}(t\text{-H})}{k_{st\text{-H}}(t\text{-H}) + k_{st\text{-D}}(t\text{-D})}\alpha_H \tag{9}$$

$$\phi_{c\text{-D}} = \phi_{\text{isc}} \frac{k_{st\text{-D}}(t\text{-D})}{k_{st\text{-H}}(t\text{-H}) + k_{st\text{-D}}(t\text{-D})}\alpha_D \tag{10}$$

At low conversion to cis, the ratio of *c*-H to *c*-D is the ratio of their initial quantum yields (eq 11). In summary of eq 11, the ratio of unlabeled to labeled product, divided by the ratio of unlabeled to labeled reactant, gives an apparent isotope effect. The apparent isotope

$$\frac{\phi_{c\text{-H}}}{\phi_{c\text{-D}}} \equiv \frac{(c\text{-H})}{(c\text{-D})} = \frac{k_{st\text{-H}}}{k_{st\text{-D}}}\frac{\alpha_H}{\alpha_D}\frac{(t\text{-H})}{(t\text{-D})} \tag{11}$$

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(14) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965.

(15) K. Sandros and H. L. J. Backstrom, *Acta Chem. Scand.*, **18**, 2355 (1964).

effect is the product of two terms, one of which is the true isotope effect on excitation transfer and the other of which is the isotope effect on partitioning of olefin triplet decay between product and reactant. For experiments starting with cis, the analogous eq 12 may be derived similarly.

$$\frac{\phi_{t\text{-H}}}{\phi_{t\text{-D}}} \equiv \frac{(t\text{-H})}{(t\text{-D})} = \frac{k_{sc\text{-H}}}{k_{sc\text{-D}}} \frac{1 - \alpha_{\text{H}}(c\text{-H})}{1 - \alpha_{\text{D}}(c\text{-D})} \qquad (12)$$

A practical difficulty to obtaining isotope effects *via* eq 12 is its implicit restriction that the conversion to product be low with respect to the amount of product that will be present at photostationary state. Since nearly all the sensitizers employed produce >80% cis at photostationary state, isotope effects starting from the cis side are intrinsically more difficult experiments. The values in Table IV in principle require correction for reverse isomerization of trans product back to cis; they are expected to be rather close lower limits.

Table IV. Isotope Effects[a] in the Isomerization of *cis*-β-Methylstyrene to *trans*-Methylstyrene

Sensitizer (E_{T}, kcal/mol)	Position of monodeuteration			
	β	α	p	m
Chrysene (56.6)	1.16 (1.15)	(0.99)	(1.03)	
Biacetyl (54.9)	1.14[b]	1.03	1.03	
Fluorenone (53.3)	1.14[b] (1.18)	1.02 (1.02)	1.03 (1.07)	
Iodine[c]	0.96			

[a] Values given are $(k_{sc\text{-H}}/k_{sc\text{-D}})[(1 - \alpha_{\text{H}})/(1 - \alpha_{\text{D}})]$ as determined by the method of eq 12. Values in parentheses are calculated from Tables III and V *via* eq 13. Precision is judged to be the same as for Table III but accuracy is probably lower; see text. [b] Lower limit; see text. Conversion was 4%. [c] Nonphotochemical experiment; see text. Hexane was employed as solvent.

A more precise way of obtaining isotope effects on the cis to trans isomerization derives from the coupling of trans to cis experiments, eq 11, with photostationary state experiments. From eq 8H and its obvious analog (8D), one can easily derive eq 13 as the photostationary state condition. Clearly determining the right-hand side of eq 13 from photostationary state experiments

$$\left.\frac{(c\text{-H})}{(c\text{-D})}\right|_{\text{PSS}} \left.\frac{(t\text{-D})}{(t\text{-H})}\right|_{\text{PSS}} = \frac{k_{st\text{-H}}}{k_{st\text{-H}}} \frac{k_{sc\text{-D}}}{k_{sc\text{-H}}} \frac{\alpha_{\text{H}}}{\alpha_{\text{D}}} \frac{1 - \alpha_{\text{D}}}{1 - \alpha_{\text{H}}} \qquad (13)$$

yields the same information, when coupled with eq 11, as does eq 12 when applied independently. The right-hand side of eq 13, given in Table V, was used to calculate the values in parentheses in Table IV. Agreement between the two is satisfactory; such deviations as exist are in the direction expected. It was not possible to study biacetyl-sensitized isomerizations in this fashion due to the slow disappearance of β-methylstyrene in these reactions.

Table V. Isotope Effects at Photostationary State[a] in the Photosensitized Isomerization of β-Methylstyrene

Sensitizer, E_{T}	Position of monodeuteration			
	β	α	p	m
Chrysene (56.6)	0.98	1.06	1.01	1.00
Fluorenone (53.3)	0.97	1.06	0.99	

[a] Values given are $(k_{st\text{-H}}/k_{st\text{-D}})(k_{sc\text{-D}}/k_{sc\text{-H}})$ as determined by the method of eq 13. Precision is judged to be the same as for Table III.

Discussion

Isotope Effect on the Decay Ratio. The observed isotope effects in Table III for propiophenone and benzophenone must be due only to the $\alpha_{\text{H}}/\alpha_{\text{D}}$ term in eq 12. This follows from the expectation that, for both of these high-energy sensitizers, $k_{st\text{-H}}$ and $k_{st\text{-D}}$ are diffusion-controlled. These rate constants therefore should be identical within the 1–2% precision of interest to us.

On this basis, $\alpha_{\text{H}}/\alpha_{\text{D}}$ is apparently 0.99 ± 0.01 for either α or β deuteration. There is thus essentially no isotope effect on the partitioning of the β-methylstyrene triplet between cis and trans; of course, this says nothing about possible identical (and thus cancelling) isotope effects on $k_{t\text{-H}}$ and $k_{c\text{-H}}$. This outcome is consistent with that obtained by Saltiel for the stilbene triplet.[16]

We conclude that the entries in Tables III and IV may be interpreted as the true isotope effects on the exitation-transfer process, so long as differences of ± 0.02 or less are not considered significant.

Direction of the Energy-Transfer Isotope Effects. Isotope effects on excitation transfer to deuterated acceptors have infrequently been observed before. Schmidt and Lee[17] have observed effects on the quenching of benzene and acetone triplets by deuterated ethylenes; $k_{\text{H}}/k_{\text{D}}$ in these cases was observed to be 1.14 and 1.18 per deuterium, respectively. For excitation transfer from benzophenone triplet to the dichloroethylene isomers, Caldwell and James[18] have observed $k_{\text{H}}/k_{\text{D}} = 1.15$ for cis and 1.18 for trans. For the β position of β-methylstyrene, we find (Tables III and IV) values of 1.13–1.18 for those sensitizers that are not expected to transfer energy at a diffusion-controlled rate; however, in those cases placing the deuterium at any other position in the conjugated system causes a significantly lower isotope effect.

The observation of direct isotope effects, rather than inverse ones, would appear to eliminate the so-called Schenck mechanism, eq 14, as the important contributor to the isomerization mechanism.[19] For eq 14a, an inverse isotope effect would certainly be expected, based on known ground-state isotope effects for additions to olefins.[1,20] Thus, the observation that iodine-catalyzed isomerization of *cis*-β-methylstyrene occurs with an isotope effect of $k_{\text{H}}/k_{\text{D}} = 0.96$ for β deuterium (Table IV) highlights the difference between triplet excitation transfer and the addition–elimination process. The

$$\text{S}^3(\equiv\text{S}\uparrow\ \uparrow) + \text{C}{=}\text{C} \longrightarrow \uparrow\text{S—C—C}\uparrow \qquad (14\text{a})$$

$$\uparrow\text{S—C—C}\uparrow \longrightarrow \text{S(S}_0) + \text{C}{=}\text{C}^3 \qquad (14\text{b})$$

$$\uparrow\text{S—C—C}\uparrow \longrightarrow \downarrow\text{S—C—C}\uparrow \longrightarrow \text{S(S}_0) + \text{C—C(S}_0) \qquad (14\text{c})$$

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(16) J. Saltiel, *J. Amer. Chem. Soc.*, **89**, 1036 (1967).

(17) M. W. Schmidt and E. K. C. Lee, *ibid.*, **90**, 5919 (1968); **92**, 3579 (1970).

(18) R. A. Caldwell and S. P. James, *ibid.*, **91**, 5184 (1969).

(19) (a) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belg.*, **71**, 781 (1962); (b) N. C. Yang, J. T. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, **90**, 3264 (1968).

(20) D. B. Denney and N. Tunkel, *Chem. Ind.* (*London*), 1383 (1959); (b) M. Matsuoka and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 1261 (1961); (c) S. Seltzer, *ibid.*, **83**, 1861 (1961); (d) T. J. Katz and R. Dessau, *ibid.*, **85**, 2173 (1963); (e) D. Van Sickle and J. O. Rodin, *ibid.*, **86**, 3091 (1964); (f) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970); (g) E. Koerner von Gustorf, D. V. White, J. Leitich, and D. Hennenberg, *Tetrahedron Lett.*, 3113 (1969).

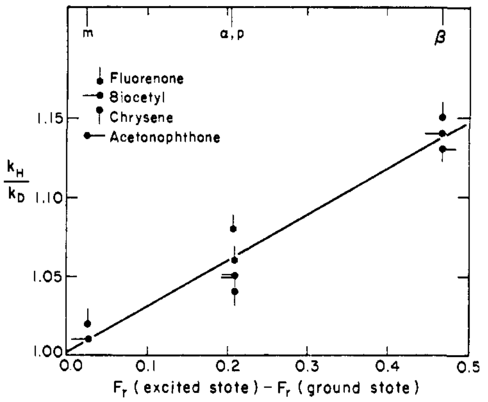

Figure 2. Correlation of isotope effect with change in free-valence index upon (vertical) excitation.

work of Bartlett[21] points out that the addition of iodine to styrene cannot be a simple iodine-atom reaction; nonetheless, the fact that it is an addition process makes it an acceptable model for eq 14. We have previously pointed out the utility of secondary deuterium isotope effects in distinguishing excitation transfer and addition–elimination processes in olefin isomerization.[18]

Dependence of the Isotope Effect on Sensitizer. The isotope effect for a given position of deuteration appears to be strikingly independent of the sensitizer for *trans-β*-methylstyrene (Table III). Note that 2-acetonaphthone and fluorenone are ketones with π–π^* lowest triplet states, chrysene is of course a π–π^* aromatic hydrocarbon triplet, and biacetyl is an n–π^* ketone triplet. We conclude that the energy transfer process does not depend critically on specific bonding between donor and acceptor. Otherwise, one surely might have expected the nature of that bonding to vary significantly within this wide range of sensitizer type. The most specific bonding might have been expected with biacetyl, since n–π^* ketone triplets and alkenes are well known to produce 1,4-biradicals (eq 14a) in other systems.[18,22]

Dependence of the Isotope Effect on the Position of Deuteration for *trans-β*-Methylstyrene. Table III summarizes the isotope effects obtained for the trans isomer. Substantial isotope effects might be expected at the β and α positions, where the isomerization occurs. However, the large para effect was at first surprising to us. We believe it to be the largest para effect known for any benzene side-chain reaction. Examples in nonphotochemical reactions are: $k_H/k_D = 0.990 \pm 0.002$ per D for the solvolysis of $(p\text{-DC}_6\text{H}_4)_2\text{CHCl}$,[23] $k_H/k_D = 1.018 \pm 0.002$ for para deuteration in the lithium cyclohexylamide catalyzed exchange of toluene-*α-d*,[24] and $k_H/k_D = 0.98 \pm 0.02$ for equilibrium acidity of the 2,6-dimethylanilinium-*4-d* ion.[1] Clearly, the para position is to be included in any consideration of the excitation transfer process.

Figure 2 shows the correlation between the isotope effects for trans and the HMO parameter ΔF_r, the change in free valence index[25] between ground and first excited state. This parameter essentially measures the "loosening" of the π bonding in *β*-methylstyrene at atom r on excitation, as can be seen from the equation $F_r(\text{excited}) - F_r(\text{ground}) = \Sigma_s[p_{rs}(\text{ground}) - p_{rs}(\text{excited})]$. The value of ΔF_r at the para and α positions is the same; the large para isotope effect is thus no anomaly.

The correlation in Figure 2 is good. It should be noted that the bond orders used refer to the planar molecule in both ground and excited state, *i.e.*, to vertical excitation. Whatever the origin of the isotope effect (*vide infra*), correlation with a parameter for vertical excitation strongly supports the conclusion reached above, from kinetic and photostationary state studies, that *trans-β-methylstyrene is a vertical acceptor of triplet excitation*. If one considered nonvertical excitation to involve a 90° twist between the p orbitals on the α and β carbons (*i.e.*, $H_{\alpha\beta} = 0$ by symmetry), the values[26] in Table VI for ΔF_r would result. Clearly the correlation with the nonvertical ΔF_r values is poor.

Table VI

Position	ΔF_r(vertical)	ΔF_r(nonvertical)
β	0.469	0.911
α	0.205	0.681
Para	0.205	0.017
Meta	0.023	~0

For *cis-β*-methylstyrene, one might expect nonvertical excitation transfer on the basis of the photostationary states in Table II and the stilbene analogy. However, neither the correlation with vertical or nonvertical ΔF_r values is successful, nor is the correlation with intermediate values. A more detailed look at possible origins of these isotope effects is required.

Possible Origins of the Isotope Effects. Several physical phenomena could in principle give rise to a direct isotope effect. We list these and include whatever indirect evidence is available in their support.

(a) These isotope effects may simply reflect a change on deuteration in the triplet excitation energy.[17] This phenomenon is well documented. The triplet excitation energy of ethylene is increased by *ca.* 50 cm^{-1} per deuterium;[27] of benzene, by 30–35 cm^{-1} per deuterium;[28] naphthalene-d_8, *ca.* 20 cm^{-1} per deuterium;[29] biphenyl-d_{10}[29] and dibenzo[*f,h*]quinoxaline-*2,3*-d_2[30] both by *ca.* 10 cm^{-1} per deuterium. On this basis, the isotope effect could be due merely to an increased activation energy for an endothermic process.

The origin of this increase in triplet excitation energy is somewhat obscure. Two possible explanations find precedent in the literature.

(1) Some vibrational frequency involving chiefly a hydrogen motion is much smaller in the excited state.[5] On this basis, a difference in the triplet excitation energy on deuteration may result from a significant difference in

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[21] (a) D. S. Trifan and P. D. Bartlett, *J. Amer. Chem. Soc.*, **81**, 5573 (1959); (b) G. Fraenkel and P. D. Bartlett, *ibid.*, **81**, 5582 (1959).

[22] (a) R. A. Caldwell, *ibid.*, **92**, 1439 (1970); (b) D. R. Arnold, *Advan. Photochem.*, 6, 301 (1968).

[23] A. Streitwieser, Jr., and H. S. Klein, *J. Amer. Chem. Soc.*, **86**, 5170 (1964).

[24] A. Streitwieser, Jr., and J. S. Humphrey, *ibid.*, **89**, 3767 (1967).

[25] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 59.

[26] E. Heilbronner and P. Straub, "Huckel Molecular Orbitals," Springer-Verlag, New York, N. Y., 1966. We may consider the 90° twist structure as having nonoverlapping benzyl and methyl radical π systems. The nonvertical ΔF_r values were obtained by comparing benzyl radical values (for α, para, and meta), or the methyl radical value (for β) with styrene ground state.

[27] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[28] G. C. Nieman and D. S. Tinti, *J. Chem. Phys.*, **46**, 1432 (1967).

[29] J. G. Calvert and J. M. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 297.

[30] E. C. Lim and Y. H. Li, *J. Chem. Phys.*, **50**, 4925 (1969).

vibrational zero point energy (ZPE), as in eq 15. For

$$E_T(D) - E_T(H) = \text{ZPE(D, excited)} - \text{ZPE(D, ground)} - \text{ZPE(H, ground)} + \text{ZPE(H, excited)} \quad (15)$$

vertical excitation, there appears to be no reason to consider in-plane modes as important contributors. The excitation only significantly affects the molecule's π system, and changes in π bonding should only affect C–C stretching frequencies among the in-plane modes. However, out-of-plane hydrogen bending frequencies might well be affected significantly; the weakening of the π bonding at a center (*i.e.*, increase in free valence index) should make out-of-plane motion of that C–H unit a lower frequency vibration. To account for an isotope effect of 1.15, the change in frequency between S_0 and T_1 for the undeuterated compound would need to be in the range of 250 cm^{-1}.[31] Moore and Pimentel,[32] in a study of out-of-plane hydrogen vibrations of $CH_2{=}X$ species, noted that examples where significant single bond character to the C–X bond existed did in fact show markedly lower out-of-plane C–H bending force constants.

(2) Deuteration may increase the strength of a π bond to which the deuterium is attached. In a study of the epr spectra of deuterated naphthalenes and benzenes,[33] Fraenkel and Lawler, *et al.*, observed that significant changes in spin density occurred at positions remote from the deuterium. The results could be accounted for satisfactorily by assuming a fractional increase $\delta\beta$ of 0.0025–0.004 in the HMO resonance integral β_0 between the deuterated and an adjacent carbon. This explanation found plausibility because the lower out-of-plane C–D vibrational amplitudes, and the expectation that the carbon 2p orbital should in part "follow" the C–D out-of-plane motion,[33] would require a larger time-averaged overlap between this 2p orbital and adjacent ones. A change of $\delta\beta = 0.003\beta_0$ would in our case correspond to *ca.* 54 cm^{-1}, since a value of $\beta_0 \cong$ 18,000 cm^{-1} is required to reconcile spectroscopic triplet energies[34] of aromatic hydrocarbons with HMO calculations.[35] The easily derived equation

$$E_T(D) - E_T(H) = 2\Delta F_r\delta\beta \qquad (16)$$

together with the value $0.003\beta_0$ allows predictions of the isotope effects on triplet excitation energy given in Table VII.

Clearly the epr results correlate semiquantitatively with the isotope effect on triplet excitation energy. The common origin of all these isotope effects seems an odds-on bet. Whether the origin resides in the increased bond strength[33] or in the differences in zero point vibrational energy[5] is less clear. The correlation we observe in Figure 2 is consistent with either origin, since either phenomenon is expected to correlate linearly with changes in π-bond strength.

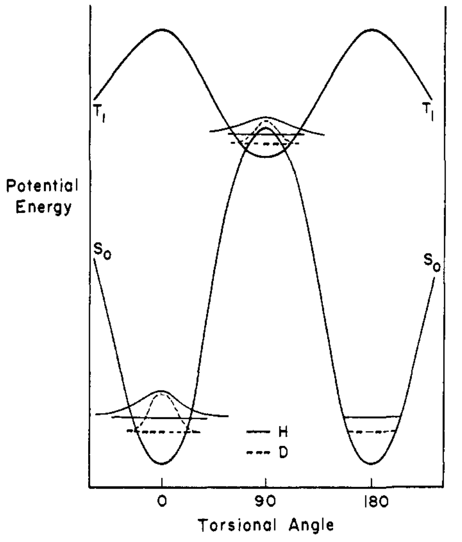

Figure 3. Schematic diagram indicating that the Franck–Condon factor between T_1 and S_0 for torsional vibration is greater for C_2H_4 than for C_2D_4: $\langle \chi_H(S_0)|\chi_H(T_1)\rangle > \langle \chi_D(S_0)|\chi_D(T_1)\rangle$.

Table VII

Compd	$E_T(D) - E_T(H)$ predicted, cm^{-1}	$E_T(D) - E_T(H)$ obsd, cm^{-1}
Ethylene-d_4	430	200
Benzene-d_6	108	200
β-Methylstyrene-β-d	51	31[a]
Naphthalene-d_8	134	150

[a] Assuming the kinetic isotope effect we observe is determined by a change in triplet excitation energy.

(b) For a nonvertical transition, the Franck–Condon factor connecting initial to final state would be significantly smaller for the deuterated system.[4,17] Changes in Franck–Condon factors on deuteration have been widely discussed[36] in connection with the deuterium isotope effect on the rate of radiationless T_1–S_0 transitions in aromatic hydrocarbons.[36]

Taking ethylene as an example of an olefin with a known[37] nonvertical excited state (D_{2h} ground state, D_{2d} excited state), Figure 3 indicates that the torsional vibrations should introduce a Franck–Condon factor significantly dependent on deuteration. Note that this is the extreme case of the dispaced and distorted oscillator, in Siebrand's terminology.[36a] The Franck–Condon factors would vary quantitatively as $\exp[-(q_0 - q)^2(\nu_0 + \nu)^{-1}]$, where $q_0 - q$ is the displacement of the oscillator and ν_0 and ν are the two vibrational frequencies, if the oscillators were harmonic. Clearly, to this approximation, the higher vibrational frequency in the case of hydrogen would give rise to a larger Franck–Condon factor than in the deuterated case. Figure 3 illustrates this point for the (0,0) component. The Franck–Condon factor will include other vibrational states in T_1 also. Anthropomorphically, the unlabeled ground state should be the one better able to "recognize" the excited-state geometry within its own range of nuclear motions.

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(31) See A. Streitwieser Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, 80, 2326 (1958), for the line of reasoning to which we draw analogy.

(32) C. B. Moore and G. C. Pimentel, *J. Chem. Phys.*, 40, 1529 (1964).

(33) R. G. Lawler, J. R. Bolton, M. Karplus, and G. Fraenkel, *ibid.*, 47, 2149 (1967). We gratefully acknowledge a discussion with Professor Lawler regarding the possible relationship of the photochemical and epr isotope effects.

(34) Reference 14, p 132; ref 29, pp 298, 301.

(35) Reference 25, p 218.

(36) (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 38, 1187 (1963); (b) W. Siebrand, *ibid*, 46, 440 (1967); (c) W. Siebrand, *ibid.*, 47, 2411 (1967).

(37) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, 41, 219 (1947).

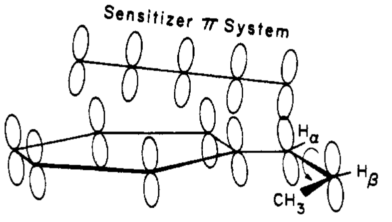
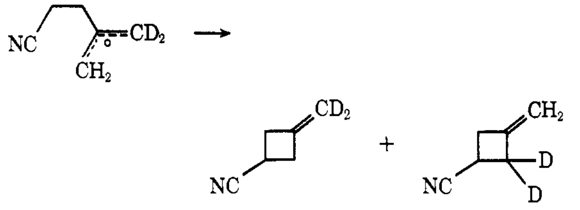
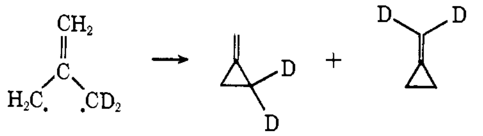


Figure 4. Possible structural model for nonvertical excitation transfer.

(c) Both the (2 + 2) thermal cycloaddition of acrylonitrile to 1,1-dideuterioallene[38] and the closure of trimethylenemethane to methylenecylcopropane[39] show significant direct isotope effects on the rotation of a $\cdots\mathrm{CH_2}$ group out of its plane, *viz.*, eq 17 and 18.



(17)



(18)

Though the origin of this isotope effect is obscure, it seems significant that the process of rotation in these systems is clearly analogous to the out-of-plane motion involved in the nonvertical excitation of an olefinic bond. Dolbier and Dai[38b] have suggested steric compression in the planar system to rationalize this isotope effect.

Nonvertical Excitation Transfer in *cis*-β-Methylstyrene. *trans*-β-Methylstyrene unequivocally appears to be a vertical acceptor, but the similarity of the β-methylstyrene and stilbene Saltiel plots suggests by analogy that *cis*-β-methylstyrene is a nonvertical acceptor. Close scrutiny of the β-methylstyrene isotope effects indeed reveals some differences between the two isomers.

The cis, para isotope effect is clearly nonzero but is too small for meaningful interpretation; it is, however, probably smaller than the trans, para isotope effect. We may restate the obvious: triplet excitation energy is important in nonvertical triplet transfer processes as well as vertical.

The large cis, β isotope effect has too many possible origins to be informative: (a) triplet excitation energy difference, (b) a Franck–Condon effect, or (c) the "rotational isotope effect."[38,39] The effect may be larger than the trans β effect (*cf.* Table V). However, there may be a small isotope effect on the triplet decay ratio, and we accordingly do not believe that this conclusion is warranted at this time. Since nonvertical processes are less sensitive than vertical processes to donor triplet excitation energy,[10,11] we feel that possibility (a) cannot explain the entire isotope effect. There is little to choose between possibilities (b) and (c), and in fact they may be closely related. There is in any case the strong similarity between the motions of the deuterated carbons in eq 17 and 18 and in nonvertical excitation transfer.

The most obvious difference appears at the α position, where $k_{st\text{-}H}H/k_{st\text{-}D} \cong 1.06$ and $k_{sc\text{-}H/sc\text{-}D} \cong 1.00$. The α position results are for cis shown most precisely by coupling the photostationary state experiments of Table V, which indicate that the trans to cis isotope effect is larger than the cis to trans isotope effect by a factor of 1.06, with the results for trans in Table III, which indicate *ca.* 1.06 as the whole isotope effect for trans to cis isomerization. If cis is also a vertical acceptor, we are unable to rationalize this difference. However, interpretation based on a nonvertical process is most informative.

Additions to double bonds show inverse isotope effects,[1,20] $k_H/k_D < 1$, at the carbon at which addition occurs. If an exciplex intermediate intervenes,[13] it is conceivable that weak bonding with the incipient benzyl radical system (α carbon plus benzene ring) is maintained until after the excitation transfer process is consummated. On this basis, the effect at the α position could conceivably be diminished as a result of a balance of this effect with the triplet excitation energy effect. Whatever the origin, Taylor and Hammond[40] observed small inverse isotope effects in fluorescence quenching of naphthalene singlets by piperylene. In this case, there is no involvement of excitation transfer. It may be that our decreased isotope effect at the α position for *cis*-β-methylstyrene and Taylor and Hammond's inverse isotope effects all have common origins related to formation of the exciplex. Figure 4 depicts a model which is consistent with all our results. Although it is tentative, we believe that it provides a useful framework from which to design further experiments to discern the nature of nonvertical excitation transfer.

Summary

Secondary deuterium isotope effects on triplet excitation have confirmed the assignment by conventional experiments that *trans*-β-methylstyrene is a vertical acceptor of triplet excitation. Similar experiments for the cis isomer have reinforced the conclusion that cis is a nonvertical acceptor. The pattern of isotope effects for cis suggests a tentative model for olefin–sensitizer interaction in a nonvertical excitation transfer process. Isotope effects are shown to be useful in studying the three questions outlined in the introductory section.

Acknowledgment. We are grateful for the financial support given by the donors of the Petroleum Research Fund (Grant No. 3031-A4) and the National Science Foundation (Grants No. GP-14796 and GP-30717). G. W. S. acknowledges a Procter and Gamble Fellowship (1968–1969).

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[38] (a) W. R. Dolbier and S.-H. Dai, *J. Amer. Chem. Soc.*, **90**, 5028 (1968); (b) S.-H. Dai and W. R. Dolbier, *ibid.*, **94**, 3946 (1972).

[39] R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

[40] G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3687 (1972).