The Quantum Chain Process in the Sensitized Cis–Trans Photoisomerization of 1,3-Dienes[1a]

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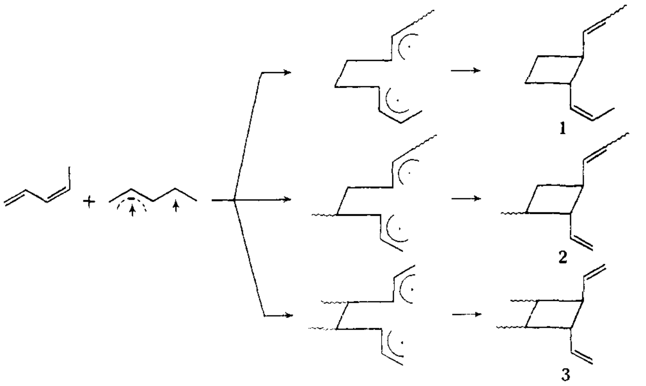
Abstract: Quantum yields for the benzophenone-sensitized cis–trans photoisomerization and dimerization of *cis*- and *trans*-1,3-pentadiene and *trans,trans*- and *cis,cis*-2,4-hexadiene have been measured at high 1,3-diene concentrations (1–10 *M*). Enhanced isomerization quantum yields are obtained for *cis*-1,3-pentadiene and the 2,4-hexadienes, but isomerization quantum yields decrease with increasing diene concentration in the case of *trans*-1,3-pentadiene. The results can be accounted for by assuming that interaction of 1,3-diene triplets with ground-state diene molecules involves two competing paths: (i) triplet excitation transfer (the quantum chain process) leading to enhanced isomerization, and (ii) biradical formation leading to dimers and diminished isomerization. The insensitivity of $\phi_{tt\rightarrow ct}/\phi_{tt\rightarrow cc}$ and $\phi_{cc\rightarrow ct}/\phi_{cc\rightarrow tt}$ ratios to diene concentration provides strong evidence in support of the quantum chain mechanism.

Excitation transfer from 1,3-diene triplets to 1,3-diene ground-state molecules leading to enhanced photoisomerization quantum yields by a quantum chain process was first postulated by Hyndman, Monroe, and Hammond for the benzophenone–2,4-hexadiene system.[2] Their observations showed that in the early stages of the irradiation a chain process obtained which led to isomerization of only one of the double bonds of the diene. At low diene concentrations, $\sim 5 \times 10^{-3}$ *M*, the results approached the requirements for two-bond isomerization mechanisms, but as the diene concentration was increased to 1.0 *M* the contribution of the chain process increased, resulting in large one-bond to two-bond isomerization quantum yield ratios, *e.g.*, $\phi_{cc\rightarrow ct}/\phi_{cc\rightarrow tt} = 94$ for 1.3 *M* *cis,cis*-2,4-hexadiene.[2] 1,3-Diene triplets were suggested to be the chain-carrying species. Our experiments with the same diene–sensitizer system over the same diene concentration range revealed no quantum yield dependence on either the irradiation time or the initial diene concentration.[3] Since the main difference in procedure was the use of freshly distilled 2,4-hexadienes in our experiments, it seems likely that distillation eliminated some photoactive impurity in the dienes which was responsible for the chain process.[3]

The possibility of the quantum chain process involving 1,3-diene triplets has more recently been suggested by Hurley and Testa to account for enhanced cis → trans quantum yields in the benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene at high diene concentrations.[4] The cis → trans quantum yield, which is known to be concentration independent in the range 0.005–0.2 *M* *cis*-1,3-pentadiene,[5] was found to increase linearly with 1,3-diene concentration in the range 1–10 *M*.[4] Since, even at the low 1,3-diene concentration range, most benzophenone triplets decay by transferring triplet excitation to the diene, $\phi_{c\rightarrow t} + \phi_{t\rightarrow c} = 1.0$,[5] the increase in $\phi_{c\rightarrow t}$ suggests that more than one *cis*-1,3-pentadiene molecule isomerizes per quantum of excitation. As an alternative to the quantum chain mechanism, a second mechanism involving addition of 1,3-pentadiene triplets to diene ground-state molecules yielding biradicals, ·D–D·, which fragment to give ground-state dienes, was also proposed.[4] A reason for concern, however, is that both mechanisms for enhanced isomerization neglect the competing formation of 1,3-pentadiene dimers.[6,7] Clearly, if the collapse of biradicals to dimers is important, reduced rather than enhanced isomerization quantum yields could result. Furthermore, the 1,3-pentadiene dimer distribution suggests that a large fraction of the biradical intermediates are formed by addition of 1,3-pentadiene triplets at the C_1 position of ground-state molecules (Scheme I).[6,7] Dimers of type **1**, **2**, and **3** are produced in yields of 52, 22, and 8%, respectively, in the benzophenone-sensitized reaction. Since allylic units are expected to retain their stereochemistry,[8,9] dissociation of biradical precursors to the major dimer products (**1**) would not result in a significant enhancement of the isomerization quantum yield.

Scheme I. Sensitized Dimerization of *cis*-1,3-Pentadiene



In an attempt to better understand the isomerization mechanism at high diene concentrations, we have

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[1] (a) Supported in part by National Science Foundation Grant No. GP-24265; (b) Alfred P. Sloan Foundation Fellow, 1971–1973.

[2] H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 2852 (1969).

[3] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

[4] R. Hurley and A. C. Testa, *ibid.*, **92**, 211 (1970).

[5] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[6] G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963).

[7] R. S. H. Liu, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1964.

[8] C. Walling and W. Thaler, *J. Amer. Chem. Soc.*, **83**, 3877 (1961).

[9] P. D. Bartlett, *Science*, **159**, 833 (1968).

studied the benzophenone-sensitized photoisomerizations of *trans*-1,3-pentadiene and *trans,trans*- and *cis,-cis*-2,4-hexadiene. We have also confirmed Hurley and Testa's observations with *cis*-1,3-pentadiene, and have measured the quantum yields of dimer formation in each case as a function of diene concentration.

Results

Benzophenone-sensitized photoisomerization quantum yields for the 1,3-pentadienes and the 2,4-hexadienes are listed in Tables I and II, respectively. 2,4-Hexadiene isomerization quantum yields for low diene concentrations (0.088–0.88 *M*) were measured using the benzophenone-sensitized photoisomerization of 1,3-pentadiene for actinometry.[5] Two sets of experiments were carried out at higher diene concentrations using different irradiation time intervals. While quantum yields for the formation of the cis,trans isomer are independent of irradiation time, accurate one-bond to two-bond isomerization quantum yield ratios could only be obtained from the longer irradiation experiments in which the conversion to the minor isomer could be readily measured. Photodimerization quantum yields are listed in Table III. Benzene was used as solvent and the benzophenone concentration was 0.05 *M* throughout. Irradiations were carried out at 30 ± 1° using the 366-nm mercury line. All irradiated samples were degassed.

Table I. Benzophenone-Sensitized Photoisomerization of the 1,3-Pentadienes[a]

Diene, *M*	$\phi_{c\to t}$	Diene, *M*	$\phi_{t\to c}$	Diene, *M*	$\phi_{t\to c}$	Diene, *M*	$\phi_{t\to c}$
0.20	0.55^{b}	0.20	0.44^{b}	4.0	0.39	8.0	0.36
1.8	0.59^{c}	0.75	0.43	5.0	0.38	9.0	0.39
5.7	0.71^{c}	2.0	0.40	5.6	0.38^{c}	9.7	0.37^{c}
9.7	0.84^{c}	3.0	0.40	7.0	0.37		

[a] Unless otherwise indicated, isomerization conversions were small and no correction was made for loss of diene due to dimerization. [b] Taken from ref 5. [c] Conversions up to 2.5%. Final diene concentrations calculated by glpc using methylcyclohexane as internal standard.

Table II. Benzophenone-Sensitized Photoisomerization of the 2,4-Hexadienes

Diene, *M*	$\phi_{tt\to ct}$	$\phi_{tt\to cc}$	ct/cc	$\phi_{cc\to ct}$	$\phi_{cc\to tt}$	ct/tt
			Run 1[a]			
0.088	0.47	0.17	2.77	0.51	0.32	1.59
0.176	0.48	0.18	2.68	0.54	0.31	1.72
0.436	0.52	0.19	2.71			
0.879	0.55	0.21	2.68	0.54	0.32	1.68
0.879	0.52	0.19	2.70			
			Run 2[b]			
1.74	0.59	0.21	2.79	0.82	0.35	2.37
2.61	0.62	0.24	2.61	0.95	0.39	2.41
3.48	0.72	0.25	2.79	0.93	0.52	1.80
4.35	0.75	0.27	2.73	1.04	0.54	1.91
6.09	0.95	0.32	2.93	1.40	0.79	1.78
6.96	0.98	0.33	2.96			
7.83	1.05	0.33	3.20	1.80	0.75	2.41
			Run 3[c]			
1.74	0.58	0.20	2.91	0.76	0.42	1.79
3.48	0.71	0.25	2.82	0.85	0.49	1.75
4.35	0.74	0.27	2.76	1.07	0.62	1.73
6.09	0.88	0.31	2.83	1.34	0.79	1.68
6.96	0.91	0.32	2.86			
7.83	0.94	0.34	2.75	1.88	1.04	1.81

[a] Performed in 3.0-ml ampoules; conversions: tt → ct, 0.8–4.7%; cc → ct, 1–4%. [b] Performed in 0.2-ml ampoules; conversions: tt → ct, 0.5–2.2%; cc → ct, <0.5%. [c] Performed in 0.2-ml ampoules; conversions: tt → ct, 1.1–4.9%; cc → ct, 1–5%.

Table III. Benzophenone-Sensitized Photodimerization of the 1,3-Pentadienes and the 2,4-Hexadienes

t-P, *M*	ϕ_D[a]	c-P, *M*	ϕ_D	tt-H, *M*	ϕ_D	cc-H, *M*	ϕ_D
4.0	0.051	3.0	0.068	2.62	0.008	2.62	0.011
6.0	0.079	4.0	0.071	4.35	0.011^{b}	4.35	0.027^{a}
8.0	0.096	5.0	0.102	6.09	0.015^{b}	5.22	0.035
9.0	0.119	6.0	0.105	6.96	0.018^{a}	6.09	0.038
		7.0	0.120	7.83	0.022^{b}	7.83	0.046
		8.0	0.141				
		9.0	0.183^{a}				

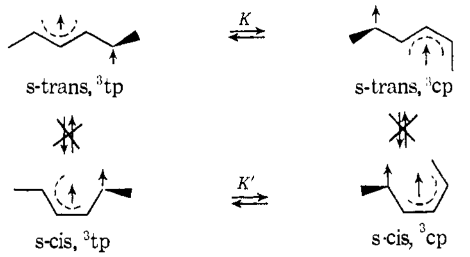
[a] Average of two independent determinations. [b] Average of three independent determinations.

In order to determine whether 1,3-pentadiene cis/trans photostationary compositions vary with 1,3-pentadiene concentration, three neat 1,3-pentadiene solutions (10.0 *M* diene, 0.05 *M* benzophenone) which were initially 0, 52, and 100% trans were subjected to prolonged irradiation. Analysis of the irradiated samples showed them to have converged to a value of 66 ± 1% trans. However, owing to competing dimerization, the total diene concentration had dropped to about 5.6 *M*.

Discussion

The present model for the geometry and the dynamic behavior of 1,3-diene triplets in solution has been inferred from sensitized photodimerization[6,7,10–12] studies at high 1,3-diene concentrations and from sensitized cis–trans photoisomerization studies[2,3,13–15] at relatively low 1,3-diene concentrations. For example, in the case of the 2,4-hexadienes two distinct noninterconvertible sets of s-cis and s-trans allylmethylene triplets are expected (Scheme II).[13,15] Equilibration between trans-twisted, ^{3}tp, and cis-twisted, ^{3}cp, triplets occurs rapidly within each set at tempera-

Scheme II. Dynamic Behavior of 2,4-Hexadiene Triplets



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(10) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

(11) D. Valentine, N. J. Turro, and G. S. Hammond, *ibid.*, **86**, 5202 (1964).

(12) W. L. Dilling, R. D. Kroening, and J. C. Little, *ibid.*, **92**, 928 (1970).

(13) J. Saltiel, A. D. Rousseau, and A. Sykes, *ibid.*, **94**, 5903 (1972).

(14) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, N. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

(15) J. Saltiel, L. Metts, A. Sykes, and M. Wrighton, *ibid.*, **93**, 5302 (1971).

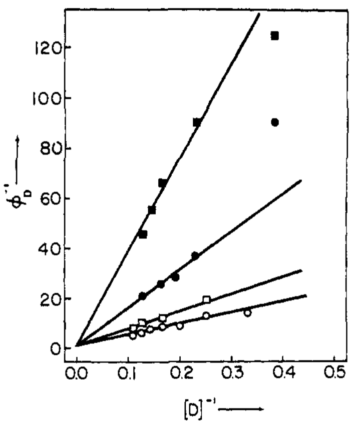


Figure 1. Variation of dimerization quantum yields with 1,3-diene concentration: (□ and ○) *trans*- and *cis*-1,3-pentadiene, respectively; (■ and ●) *trans,trans*- and *cis,cis*-2,4-hexadiene, respectively.

tures higher than 135°K.[13] High triplet excitation donors like benzophenone provide entry predominantly into the s-trans set of 1,3-diene triplets.[13,15] In each s-trans triplet the allylic moiety retains its stereochemistry, but the twisted ends upon intersystem crossing give cis and trans double bonds with equal probability. The deviation of the overall decay process from the random distribution of tt:tc:cc of 1:2:1 is attributed to a smaller than unity equilibirum constant K in Scheme II.[13]

A mechanism which includes both processes suggested to account for enhanced sensitized photoisomerization of 1,3-dienes at high diene concentrations is shown for *cis*-1,3-pentadiene in eq 1-7, where **B**, c, and t represent benzophenone, *cis*-, and *trans*-1,3-pentadiene, respectively, a is the intersystem crossing efficiency of **B**, ^{3}p represents all equilibrating s-trans

$$\mathrm{B} \xrightarrow{h\nu} {}^1\mathrm{B} \xrightarrow{a} {}^3\mathrm{B} \qquad (1)$$

$$^3\mathrm{B} + \mathrm{c} \xrightarrow{k_1} {}^3\mathrm{p} + \mathrm{B} \qquad (2)$$

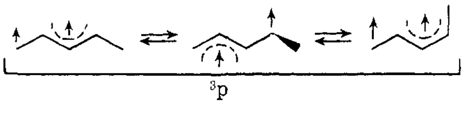
$$^3\mathrm{p} \xrightarrow{k_2} \alpha\mathrm{t} + (1 - \alpha)\mathrm{c} \qquad (3)$$

$$^3\mathrm{p} + \mathrm{c} \xrightarrow{k_3} \cdot\mathrm{D{-}D}\cdot \qquad (4)$$

$$^3\mathrm{p} + \mathrm{c} \xrightarrow{k_4} \alpha\mathrm{t} + (1 - \alpha)\mathrm{c} + {}^3\mathrm{p} \qquad (5)$$

$$\cdot\mathrm{D{-}D}\cdot \xrightarrow{k_5} \text{dimers} \qquad (6)$$

$$\cdot\mathrm{D{-}D}\cdot \xrightarrow{k_6} (2 - \beta)\mathrm{t} + \beta\mathrm{c} \qquad (7)$$



diene triplets, and α and $(2 - \beta)$ with $\beta < 1$ are the fractions of trans isomer obtained from the triplets and the biradicals, respectively. For small conversions, the dependence of dimerization and isomerization quantum yields on *cis*-1,3-pentadiene concentration is described by eq 8 and 9.

$$\phi_\mathrm{D} = \left(\frac{k_5}{k_5 + k_6}\right)\left(\frac{k_3[\mathrm{c}]}{k_2 + k_3[\mathrm{c}]}\right)a \qquad (8)$$

$$\phi_{\mathrm{c}\rightarrow\mathrm{t}} = \frac{a}{k_2 + k_3[\mathrm{c}]}\left(\alpha(k_2 + k_4[\mathrm{c}]) + \frac{k_6}{k_5 + k_6}(2 - \beta)k_3[\mathrm{c}]\right) \qquad (9)$$

Photodimerization. According to eq 8, plots of the inverse of the dimerization quantum yields *vs.* the inverse of the diene concentrations should be linear with the intercepts giving $(k_5 + k_6)/ak_5$ and the slope to intercept ratios giving k_2/k_3 for each diene. The photodimerization data are plotted in this way in Figure 1. It can be seen that with the exception of the photodimerization quantum yields obtained for the lowest concentration of each 2,4-hexadiene, the adherence of the data to the expected linear relationships is adequate.[16] The points for each line are consistent with an intercept of unity and the lines are so drawn. Since the intersystem crossing efficiency of benzophenone, a, is unity,[5] this would require that with each diene all adduct biradicals give dimers, *i.e.*, $k_5 \gg k_6$. While the present dimerization data are not sufficiently precise to rigorously require this conclusion, it is reassuring to note that the same result has been obtained from the detailed studies of the benzophenone-sensitized dimerization of isoprene[10] and 1,3-cyclohexadiene.[17] As will be shown below, the 2,4-hexadiene photoisomerization data provide strong evidence for neglecting bond breaking as contributing significantly to the fate of biradicals.

Values of k_3/k_2 obtained from the lines in Figure 1 are listed in Table IV. These values can be compared with a corresponding ratio in the isoprene system of $6.2 \times 10^{-2}\ M^{-1}$.[10] Barring large differences between the triplet decay rate constants for these acyclic 1,3-dienes, the k_3/k_2 ratios indicate that biradical formation is inhibited by methyl substitution at the terminal positions of the diene system.

Table IV. Rate Constant Ratios for 1,3-Diene Triplets

1,3-Diene	k_3/k_2, M^{-1}	k_4/k_2, M^{-1}
trans-1,3-Pentadiene	1.4×10^{-2}	0
cis-1,3-Pentadiene	2.2×10^{-2}	0.10
trans,trans-2,4-Hexadiene	2.6×10^{-3}	0.16
cis,cis-2,4-Hexadiene	6.4×10^{-3}	0.31

Photoisomerization. Assuming $k_5 \gg k_6$, eq 9 can be rewritten as eq 10, where $a = 1.0$ for benzophenone

$$(\phi_{\mathrm{c}\rightarrow\mathrm{t}}/\phi_{\mathrm{c}\rightarrow\mathrm{t}}{}^0)(1 + k_3[\mathrm{c}]/k_2) = 1 + k_4[\mathrm{c}]/k_2 \qquad (10)$$

and $\phi_{\mathrm{c}\rightarrow\mathrm{t}}{}^0 = \alpha$ in dilute solutions.[5] Expressions analogous to eq 10 can be derived for each of the other three dienes. The quantities on the left-hand side of these expressions are plotted *vs.* 1,3-diene concentration in Figures 2 (1,3-pentadienes) and 3 (2,4-hexadienes). The quantum yields reported by Hurley and Testa[4] are included in Figure 2 and are somewhat higher than our values. The deviation is probably due to our having corrected the *cis*-1,3-pentadiene

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[16] The deviation of the two points from the lines is probably due to the uncertainty in measuring the very small conversions to dimer in these two cases.

[17] G. F. Vesley, Ph.D. Thesis, California Institute of Technology, Pasadena, Calif., 1968.

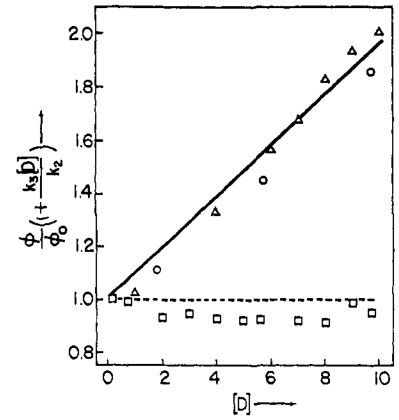


Figure 2. Dependence of isomerization quantum yields on 1,3-pentadiene concentration, corrected for dimerization: (□) trans → cis; (○) cis → trans; (△) cis → trans from ref 4.

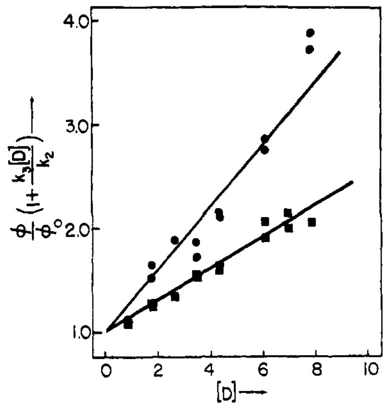
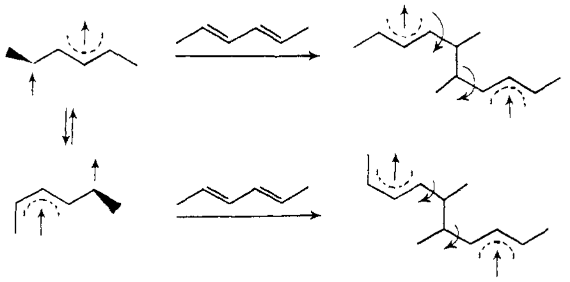


Figure 3. Dependence of isomerization quantum yields on 2,4-hexadiene concentration, corrected for dimerization: (■) trans, trans → cis,trans; (●) cis,cis → cis,trans.

data for 1,3-pentadiene loss, a procedure which according to ref 4 results in ~10% lower quantum yields. It can be seen from Figures 2 and 3 that the concentration dependence of trans → cis quantum yields is due entirely to competing dimerization,[18] while for the cis → trans direction in 1,3-pentadiene and both directions in the 2,4-hexadienes, correction for dimer formation reveals increased roles for the enhanced isomerization process. Values of k_4/k_2 obtained fom the slopes in Figures 2 and 3 are listed in Table IV. Although some contribution to enhanced isomerization in *cis*-1,3-pentadiene by biradical cleavage, step 7, cannot be rigorously ruled out on the basis of the 1,3-pentadiene data, the observations with the 2,4-hexadienes show that isomerization *via* biradicals must be unimportant. Likely adduct biradicals in the *trans,trans*-2,4-hexadiene–benzophenone system are shown in Scheme III. Since the allylic units in these biradicals are expected to retain their stereochemistry,[8,9,19] only one-bond isomerization can be anticipated in the second diene moiety. Participation of the biradicals in isomerization should, therefore, be reflected in increased $\phi_{tt\rightarrow tc}/\phi_{tt\rightarrow cc}$ and $\phi_{cc\rightarrow tc}/\phi_{cc\rightarrow tt}$ ratios. The data in Table II show that whereas absolute isomerization quantum yields increase more than twofold over the concentration range studied, one-bond to two-bond isomerization quantum yield ratios do not change, $\phi_{tt\rightarrow tc}/\phi_{tt\rightarrow cc} = 2.8 \pm 0.1$, $\phi_{cc\rightarrow tc}/\phi_{cc\rightarrow tt} = 1.7 \pm 0.1$. It should be noted that this insensitivity of the quantum yield ratios to changes in diene concentration dissociates our observations from those of Hyndman, *et al.*,[2] and provides strong evidence in support of the quantum chain mechanism for enhanced isomerization.

Scheme III. Biradical Formation in the *trans,trans*-2,4-Hexadiene–Benzophenone System



A further simple argument against the involvement of biradicals in isomerization enhancement can be based on the magnitude of the isomerization quantum yields obtained at high hexadiene concentration. The maximum isomerization enhancement which could be reasonably attributed to the biradical mechanism would arise if all diene triplets gave biradicals and if all biradicals cleaved to dienes, eq 11, with complete

$$\text{D–D}\cdot \longrightarrow \alpha'\text{tt} + \beta'\text{tc} + (2 - \alpha' - \beta')\text{cc} \qquad (11)$$

loss of stereochemistry at each double bond. Under these extreme conditions the isomerization quantum yields would be equal to the decay fractions in eq 11, *e.g.*, $\phi_{cc\rightarrow tt} = \alpha'$, $\phi_{cc\rightarrow tc} = \beta'$, and $\phi_{tt\rightarrow cc} = 2 - \alpha' - \beta'$, and the maximum sum of $\phi_{cc\rightarrow tt} + \phi_{cc\rightarrow tc} + \phi_{tt\rightarrow cc}$ would be 2. Examination of the observed quantum yields in Table II, run 3, shows that the sum of these three quantum yields exceeds this limit, being 3.3 at 7.8 *M*.

The observation of isomerization enhancement in *cis*- but not in *trans*-1,3-pentadiene may be due to the lower triplet excitation energy of the cis isomer. The lowest spectroscopically observed vibrational bands in the $^1\text{T} \leftarrow {}^0\text{S}$ transitions of the 1,3-pentadienes are at 59.2 and 57.3 kcal/mol for the trans and the cis isomer, respectively.[21] Preferential excitation transfer to the cis isomer of 1,3-pentadiene by sensitizers in the 61–56-kcal/mol range has also been proposed to account for the higher trans/cis photostationary ratios obtained in their presence.[14] It may also be argued that enhancement in isomerization by a quantum chain process in *trans*-1,3-pentadiene could be less effective because the initially produced *s-trans*-1,3-diene triplets might seek out ground-state molecules

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[18] While the small deviations of the corrected relative trans → cis quantum yields from unity are probably within our experimental error, they may be due in part to minor competing side reactions, *e.g.*, addition of benzophenone triplets to the diene (J. A. Barltrop and H. A. J. Carless, *J. Amer. Chem. Soc.*, **93**, 4794 (1971)) and/or formation of higher diene polymers (see Experimental Section).

[19] Our observation that benzophenone sensitization gives different dimer distributions starting with *cis*- and *trans*-1,3-pentadiene provides additional evidence requiring retention of stereochemistry in the allylic moieties of the biradicals. The same conclusion can be drawn from the structural differences of adducts arising from the addition of 1,2-benzanthracene triplets to *cis*- and *trans*-1,3-pentadiene.[20]

[20] (a) J. Saltiel, *et al.*, *Org. Photochem.*, **3**, 1 (1973); (b) J. Saltiel, D. E. Townsend, L. Metts, and M. Wrighton, unpublished observations.

[21] R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).

in s-cis conformations in the energy transfer step. This is an attractive possibility on energetic grounds and since s-cis triplets decay predominantly to *trans*-1,3-pentadiene,[15] a smaller isomerization enhancement would be expected. However, this possibility can be discarded for two reasons: (i) diene dimer compositions do not change with diene concentration and (ii) the insensitivity of $\phi_{tt\rightarrow tc}/\phi_{tt\rightarrow cc}$ ratios to changes in 1,3-diene concentration rules out the involvement of s-cis triplets in the quantum chain process in *trans,trans*-2,4-hexadiene.

Evidence suggesting excitation transfer from isoprene triplets to azulene,[10] 9,10-dibromoanthracene,[7] and the stilbenes,[22] and from 1,3-cyclohexadiene triplets to azulene,[17] has been presented. In the case of *trans*-1,1-dimethyl-1-benzoyl-2,4-pentadiene (**4**), where diene triplets are efficiently produced *via* intramolecular excitation transfer from the $^3(n,\pi^*)$ state of the benzoyl moiety, several potential triplet excitation acceptors, including azulene, were shown to have no effect on either trans/cis photostationary state compositions or on trans → cis isomerization quantum yields.[23] It was concluded that the rate constants for intramolecular triplet excitation transfer in **4** and for relaxation of the "planar" 1,3-diene triplet to distorted configurations must be larger than 2×10^9 sec^{-1}.[23] Also, if by analogy with the observations obtained with isoprene[10] it is assumed that vibrationally relaxed 1,3-diene triplets of **4** transfer triplet excitation to azulene, it can be concluded that this nonvertical excitation transfer process gives the same ratio of cis and trans isomers as does natural radiationless decay.[23] The triplet excitation transfer step which we have proposed, eq 5, similarly gives ground-state dienes in the same ratio as does natural decay. This is required by the insensitivity of 2,4-hexadiene product ratios to diene concentration and suggests that trans-twisted and cis-twisted allylmethylene triplets transfer triplet excitation to ground-state diene molecules with equal efficiency. Since the enthalpy difference between the two isomeric conformations of *s-trans*-2,4-hexadiene triplets appears to be only 300 cal mol^{-1},[13] the equality of the α's in eq 3 and 5 is not surprising. Generally, different α's in eq 3 and 5 should be expected in cases involving substantially different isomeric distorted triplets or in cases in which planar triplets can become involved in the excitation transfer step either because their energy is similar to that of the distorted triplets or because the distortion from planar to twisted conformations is slow. It is interesting to note in this connection that a quantum chain process in which the excitation transfer step(s) give(s) olefins in different ratio than does natural decay probably accounts for the concentration dependence of photostationary states[24] and quantum yields[25] observed in the benzophenone-sensitized photoisomerization of 1,3,5-trienes.

Limiting values for the rate constants k_4 can be based on observations concerning the benzophenone-sensitized photodimerization of isoprene.[10] The quenching of the dimerization by azulene gives $k_7/k_3 = 1.2 \times 10^3$ where k_7 is the rate constant for the transfer of triplet excitation from *s-trans*-isoprene triplets to azulene (eq 12).[10] Using the value of $k_3/k_2 = 6.2$

$$^3\mathrm{p} + \mathrm{Az} \xrightarrow{k_7} {}^3\mathrm{Az} + \text{isoprene} \qquad (12)$$

$\times 10^{-2}$ M^{-1} in isoprene, it follows that $k_7/k_2 = 75$ M^{-1}. An increase of the viscosity of the medium was shown to have no significant effect on isoprene dimerization quantum yields obtained with benzophenone as the sensitizer in the presence or absence of azulene,[10] suggesting that neither the addition of isoprene triplets to diene molecules nor their interaction with azulene are diffusion controlled, *i.e.*, $k_7 \leq 6 \times 10^9$ M^{-1} sec^{-1}.[10] This places an upper limit to the rate constant for decay of *s-trans*-isoprene triplets of $k_2 \leq 8 \times 10^7$ sec^{-1}. Assuming that the rate constants for decay of *s-trans*-1,3-pentadiene and 2,4-hexadiene triplets are similar to that for isoprene triplets, it follows that $k_4 \leq 2.5 \times 10^7$ M^{-1} sec^{-1}. For a vertical triplet excitation transfer process in solution a rate constant of 2.5×10^7 M^{-1} sec^{-1} is consistent with an endothermicity for the process of ~3.3 kcal/mol.[26,27] A somewhat larger endothermicity could be tolerated if the excitation transfer process is nonvertical.[27] Although a large number of assumptions is involved, the occurrence of step 5 suggests that the amount of stabilization achieved by the distortion of planar 1,3-diene triplets to the twisted equilibrium geometries ^{3}p, although small, is probably larger than 3 kcal/mol.[28]

Experimental Section

Materials. *cis*-1,3-Pentadiene (c) and *trans*-1,3-pentadiene (t), research grade from Aldrich, and *cis,cis*-2,4-hexadiene (cc) and *trans,trans*-2,4-hexadiene (tt), from Columbia Organic Chemicals Co., were bulb-to-bulb distilled immediately prior to use. Initial compositions of the 2,4-hexadienes were: 0.06% cc, 0.32% ct, 99.62% tt; 0.91% ct, 99.09% cc. Initial compositions of the 1,3-pentadienes were: 99.91% t, 0.09% c; 99.93% c, 0.07% t. Diene dimers were present in *trans*-1,3-pentadiene, 0.22%, but could not be detected in the other diene samples. Benzophenone, Fischer reagent grade, was recrystallized three times from pentane and sublimed under reduced pressure. Benzene, Fischer "Spectranalyzed" grade, and carbon tetrachloride, Baker spectral grade, were used without purification.

Analytical Procedures. Determinations of isomeric diene compositions were by glpc on a 20 ft × $^1/_8$ in. column gradient packed with segments of 40, 30, 20, and 10% β,β-oxydipropionitrile on Chromosorb P. Aerograph Models 600-C and 600-D Hi-Fi were employed. Column temperatures were 25 and 50° for analysis of the 1,3-pentadienes and 2,4-hexadienes, respectively. Analyses of the 1,3-pentadiene and 2,4-hexadiene dimers were by glpc on a 5 ft × $^1/_8$ in. column packed with 20% Carbowax 20M on Chromosorb P, or on a 5 ft × $^1/_8$ in. column packed with 5% SE-30 on Chromosorb W. Column temperatures were 90° except for the 2,4-hexadiene dimers on the Carbowax column, for which the temperature was 100°. Benzene was evaporated by blowing a slow stream of nitrogen over the samples. Carbon tetrachloride was added prior to analysis. *n*-Dodecane was used as internal standard for determining concentrations of both 1,3-pentadiene and 2,4-

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[24] R. S. H. Lui, *Pure Appl. Chem.*, *Suppl.* (*23rd Congr.*), 1, 335 (1971).

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[28] Following the submission of this paper an article appeared dealing with the sensitized photoisomerization of the 1,3-pentadienes in which the biradical mechanism is advocated to account for observations at high diene concentration.[29] As discussed above this mechanism, being inconsistent with our observations, can be ruled out. We wish to thank Professor Vesley for helpful correspondence concerning his published[29] and unpublished[30] work in this area.

[29] G. F. Vesley, *Mol. Photochem.*, 4, 519 (1972).

[30] G. F. Vesley and S. J. Susag, unpublished observations.

hexadiene dimers, but a set of 2,4-hexadiene experiments was also carried out using *n*-tetradecane as internal standard. The detector response ratio was assumed to be the ratio of the number of carbons in the standard to that in the dimer. For the *n*-dodecane–1,3-pentadiene dimer system a response ratio of 1.18 ± 0.02 was measured experimentlly which was in excellent agreement with the expected ratio of 1.20. The 1,3-pentadiene dimers used in this determination were obtained from the benzophenone-sensitized photodimerization of neat 1,3-pentadienes. The benzophenone was removed by chromatography on alumina using *n*-pentane as the eluent and the dimers were distilled prior to use. The distillation step was essential since omitting it gave a *n*-dodecane–dimer response ratio of 1.43, suggesting the presence of higher boiling side products in the dimers.[18] Deviations of independently measured dimer quantum yield values were in most cases $\leq 5\%$ of the average values reported in Table III, and only in one case was the deviation as large as 10%. Diene concentrations were determined using methylcyclohexane as internal standard on a 15 ft × 1/8 in. column packed with 25% Ucon (Polar) on Chromosorb P.

Irradiation Procedures. Irradiations of high diene concentration samples (0.2-ml solution) were performed in a miniature merry-go-round apparatus which has previously been described.[13] Other irradiations, including run 1 in Table II, were performed in a conventional merry-go-round apparatus[31] (3-ml solution) employing 200- or 450-W Hanovia high-pressure mercury lamps. Corning filters CS 7-37 and CS 0-52 were used to isolate the 366-nm mercury line. All irradiations were carried out at 30 ± 1°. Samples were degassed to $<10^{-5}$ Torr using six freeze–pump–thaw cycles and sealed. The benzophenone-sensitized photoisomerization of *cis*-1,3-pentadiene at low diene concentration was used for actinometry.[5] The extinction coefficient of benzophenone at 366 nm in neat 1,3-pentadiene, 69, was found to be the same as in benzene solution.

Acknowledgment. We thank Mr. W. Greene for initial determinations of 1,3-pentadiene dimerization quantum yields and Dr. A. K. Uriarte for measuring the extinction coefficient of benzophenone in 1,3-pentadiene and for helpful discussions.

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Cage Effects in the Photochemistry of (*S*)-(+)-2-Phenylpropiophenone[1]

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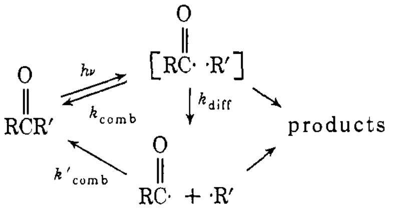
Abstract: Irradiation of (*S*)-(+)-2-phenylpropiophenone (**1**) in benzene in the presence of dodecanethiol scavenger leads to the formation of benzaldehyde ($\Phi = 0.44$) and racemized ketone **1** ($\Phi = 0.33$). The quantum inefficiency (~20%) is attributed to cage recombination of the benzoyl–1-phenylethyl radical pair prior to loss of chirality rather than to radiationless triplet decay. It is concluded that the rate of radical pair cage reactions is comparable to the rates for diffusion or rotation of the 1-phenylethyl radical with respect to the benzoyl radical.

The photochemical α-cleavage (type I) reaction of ketones in the solution phase normally occurs with quantum efficiencies significantly less than unity.[2–4] For example, we have investigated the α cleavage of a number of *tert*-alkyl[2] and benzyl phenyl ketones[3] and find maximum quantum yields for product formation less than 0.5 in all cases. Such low efficiencies may be due in part to cage (k_{comb}) and noncage (k'_{comb}) recombination of the initially formed radical pair (eq 1). Several recent reports of polarization of the parent ketone nmr spectrum upon irradiation have provided evidence for the cleavage–recombination process.[5]



(1)

However, the extent of cage and noncage recombination cannot be determined from CIDNP spectra. Yang[4c] and Bartltrop[4d] have established the importance of cleavage–recombination for cycloalkanones which undergo photoepimerization at the α carbon as well as isomerization *via* a biradical intermediate. The role of radical pair recombination in acyclic ketone photochemistry is more difficult to assess as both cage and random phase reactions occur.[6] As one approach to this problem, we have investigated the photochemistry of (*S*)-(+)-2-phenylpropiophenone (**1**).[7] This system was chosen because of our interest in benzyl phenyl ketones[3] and, moreover, because the CIDNP results of Müller and Closs[5c] on (±)-**1** qualitatively established the occurrence of cage recombination.

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