Table I. Quantum Yields for Products from 1,3-Pentadienes[a]

M	Quantum yields × 10^3		
cis	3-Methyl-cyclobutene	*trans*-1,3-Pentadiene	1,3-Dimethyl-cyclopropene
2.85	3.4	110	0.67
2.42	3.4	100	0.70
1.75	3.4	100	0.75
1.34	3.3	100	0.78
0.89	3.4	100	0.80
0.60	3.3	100	0.82
0.00	**3.4**	**100**	**0.88**
trans	3-Methyl-cyclobutene	*cis*-1,3-Pentadiene	1,3-Dimethyl-cyclopropene
2.02	30	84	1.2
1.57	30	83	1.3
1.29	31	84	1.4
0.99	31	84	1.5
0.70	30	83	1.6
0.41	30	81	1.6
0.00	**30**	**83**	**1.9**

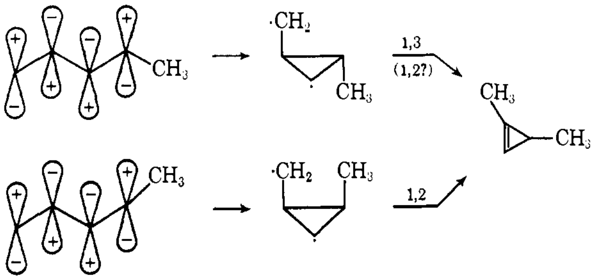
[a] Wavelength 253.7 nm; intensity 8.03×10^{-7} einstein sec^{-1}; solvent cyclohexane; ambient room temperature.

the ease that has been reported for the triplet excited states.

The effect that the structures of the stereoisomers have on the course of the cyclizations can be explained in the following way. In the formation of 3-methylcyclobutene, which is presumably a concerted process,[5] the methyl group may constitute a steric hindrance to the closure when the molecule has a *cis* configuration.

The tenfold difference in rate between the excited states of *cis*- and *trans*-1,3-pentadiene may mean that both are well removed from the configuration at the energy minimum in which a 90° rotation about the C_3–C_4 bond has occurred.

The photoisomerization to cyclopropenes is best explained in terms of the diradical intermediate that was previously proposed.[1] The excited states of the *cis*- and *trans*-1,3-pentadienes can be visualized as giving rise to different diradicals (the sense of the closure seems unimportant). The diradical derived from the *cis* can give the cyclopropene only by a 1,2 shift of an H atom, but a similar process can also give 2-methylmethylenecyclopropane, a product which actually is formed, in a yield comparable to that of 1,3-dimethylcyclopropene, in the irradiation of *cis*-1,3-pentadiene.[6] That derived from *trans* can give a cyclopropene not only by a similar 1,2-hydrogen shift but also by a 1,3-hydrogen shift which seems to be the uniquely preferred pathway for cyclopropene formation in 1,3-butadiene and isoprene.[1] It may also be noted that the diradicals do not have any simple pathway for interconversion which is consistent with the low quantum yield for stereoisomerization.



Since the energy profile (as a function of angle of rotation) between the perpendicular state and the *cis* or *trans* isomers of any olefin in their excited singlet state does not contain any barrier,[7] the difference in photochemical reactivity between the *cis* and *trans* forms that is observed here becomes understandable only if the lifetimes of these excited states[8] are quite small—possibly of the order of the time for a rotation about the C_3–C_4 bond in 1,3-pentadiene. The short radiative lifetimes of the excited singlet states of linear 1,3-dienes, coupled to their failure to fluoresce,[9] make this a very real possibility.

---

tion of 1,3-dimethylcyclopropene. No 3-methylcyclobutene was formed from either isomer.

(5) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

(6) The total absence (within experimental uncertainty) of 2-methylmethylenecyclopropane as a product from *trans*-1,3-pentadiene is significant since it underscores the possibility of two distinct diradical intermediates being formed from *trans*- and *cis*-1,3-pentadienes, *i.e.*, a two-step rather than a concerted mechanism for the formation of 1,3-dimethylcyclopropene.

(7) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(8) In this study, we have compared the quantum yields for two cyclization reactions from the *cis* and *trans* isomers and tacitly equated them to the ratio of the rate constants for these processes (*i.e.*, k_5/k_6). This equality is true only if the ratio of the rate constants for all processes (or just the unimolecular processes at infinite dilution) from the *cis* and the *trans* isomers is unity; in turn it means that the ratio of the lifetimes of their singlet excited states is unity under identical experimental conditions. Since 90% of the time both species return unchanged to the ground state, these assumptions seem warranted.

(9) R. Srinivasan, *Advan. Photochem.*, **4**, 119 (1966).

(10) Postdoctoral Fellow, 1968–present.

S. Boué,[10] R. Srinivasan
IBM T. J. Watson Research Center
Yorktown Heights, New York 10598

Received February 20, 1970

The Direct *cis–trans* Photoisomerization of 1,3-Dienes in Solution

Sir:

Evidence has been presented which shows that the benzophenone-sensitized photoisomerization of the 2,4-hexadienes in solution proceeds *via* common triplet-state diene intermediates, with transfer of triplet excitation to any of the three diene isomers leading to isomerization at both double bonds.[1] The results could be explained by assuming either a 1,4-biradical geometry for the common triplet state or the intermediacy of two rapidly equilibrating triplets of the allylmethylene type.[1–3] Direct excitation of the 2,4-hexadienes in diethyl ether solution has been reported to yield *cis–trans* interconversion as well as valence isomerization.[4] Of particular interest is the suggestion that intermediates of the cyclopropylmethylene type, **1**, are produced reversibly and are precursors of bicyclobutane, cyclopropene, and dimeric products.[4] Clearly, intermediates of type **1** provide a mechanism for *cis–*

1

---

(1) J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969).

(2) H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *ibid.*, **91**, 2852 (1969).

(3) E. M. Evleth, *Chem. Phys. Lett.*, **3**, 122 (1969).

(4) R. Srinivasan, *J. Amer. Chem. Soc.*, **91**, 4498 (1969).

trans photoisomerization whereby absorption of one quantum of light would lead to isomerization of only one of the double bonds. The following concerns an experimental test of this mechanism.

The photoisomerizations of *trans,trans*- (*tt*), *cis,trans*- (*ct*), and *cis,cis*-2,4-hexadiene (*cc*) were studied in pentane solution, 0.09 *M*. The source of the dienes and the analytical procedure have been described.[1] Quantum yield irradiations, 2537 Å, were carried out in parallel at 30° in a merry-go-round apparatus[5] using a Nester–Faust low-pressure mercury lamp whose output was filtered through Vycor and chlorine gas. Samples were degassed to $<10^{-5}$ mm. Acetone-sensitized *cis* → *trans* photoisomerization of 2-pentene was used for actinometry.[6]

The photoisomerization quantum yields are given in Table I. A large fraction of the $\phi_{tt \to cc}$ and $\phi_{cc \to tt}$ values can be attributed to second quantum isomerization involving formation of the intermediate *ct* isomer as a first step. In agreement with previous results,[4] in the case of the *tt* isomer geometric *trans* → *cis* photoisomerization was accompanied by the formation of *cis*-3,4-dimethylcyclobutene as a minor primary product, ϕ = 0.024. With this minor exception there was no detectable decrease in the total diene concentrations during the irradiation periods employed for quantum yield measurements. The 2,4-hexadiene photoequilibrium composition was found to be 40.6% *tt*, 26.4% *ct*, and 33.0% *cc*. Direct vapor-phase irradiation of a mixture of the 2,4-hexadienes at ±2537 Å was shown to yield 1,3-hexadiene as a major product.[7] This product is not formed upon irradiation in solution and may arise from vibrationally excited intermediates.

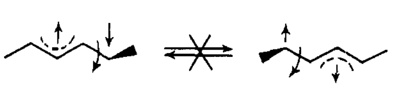
Table I. Quantum Yields of Direct 2,4-Hexadiene Isomerization[a]

$\phi_{tt \to ct}$	$\phi_{cc \to ct}$	$\phi_{ct \to tt}$	$\phi_{cc \to tt}$	$\phi_{ct \to cc}$	$\phi_{tt \to cc}$	$\Sigma\phi$
0.37	0.41	0.17	<0.03	0.29	<0.03	1.31

[a] Corrected for back reaction; no decrease in total diene concentration relative to internal standard, glpc. Conversions were less than 5%.

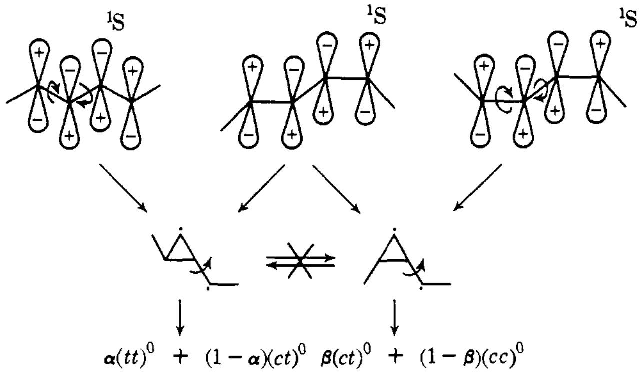
The striking difference between the quantum yields in Table I and those obtained for the benzophenone-sensitized photoisomerization of the 2,4-hexadienes[1] shows that different *cis–trans* isomerization paths obtain for singlet and triplet diene excited states. A common 1,4-biradical singlet-state intermediate has been excluded. A minimum of two distinct intermediates each leading to isomerization of only one double bond is required in order to account for the results in Table I. The small values of $\phi_{cc \to tt}$ and $\phi_{tt \to cc}$ show that more than 90% of the excited diene molecules bypass the triplet manifold, so that $\phi_{IS} < 0.1$. This conclusion is in agreement with studies of other 1,3-dienes, showing that $S^1 \to T$ intersystem crossing in such systems is very inefficient.[8-11]

The *cis–trans* isomerization results can be accounted for by excited singlets of the allylmethylene type[1,2] provided their interconversion is too slow to compete with decay to the ground state (eq 1). Concerted formation of cyclopropylmethylene type biradicals which give back diene ground states provides an alternative, and perhaps more attractive, interpretation of the results. The mechanism for the isomerization involving these intermediates is shown in Scheme I. The above mechanisms represent an oversimplification since they disregard excitation of dienes in *s-cis* conformations. That such excitation is surely occurring in the case of the *tt* isomer is indicated by the preferential formation of *cis*-3,4-dimethylcyclobutene from that isomer. It should be noted that starting with any of the three isomers more than 50% of the excited molecules decay without undergoing *cis–trans* isomerization. An analysis of the quantum yields in Table I will be given in the full paper. It can be concluded that (1) the formation of the intermediates leading to isomerization is not completely efficient so that it competes with decay to the starting dienes, or (2) if the intermediates are formed efficiently, their lifetimes are not sufficiently long to permit complete randomization with respect to rotation about the methylene single bond.



(1)

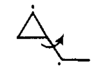
Scheme I. The Cyclopropylmethylene Mechanism for *cis–trans* Isomerization



Direct excitation of the 1,3-pentadienes gives relatively inefficient *cis–trans* isomerization, $\phi_{c \to t}$ = 0.091, $\phi_{t \to c}$ = 0.115. Interpreted by the cyclopropylmethylene mechanism this inefficiency suggests that formation of biradicals **2** and **3**, which cannot undergo *cis–trans* isomerization, is preferred to the formation of diradical **4**, which can.[12] Experiments involving the 1-deuterio-

2

3



4

---

[5] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

[6] J. Saltiel, K. R. Neuberger, and M. Wrighton, *J. Amer. Chem. Soc.*, 91, 3658 (1969).

[7] The deaerated dienes were bulb to bulb distilled through the irradiation flask. The Nester–Faust lamp output was filtered through quartz only, but more than 90% of the incident radiation was at 2537 Å. The 1,3-hexadiene was identified by comparison with authentic material (Aldrich), but its stereoisomeric composition has not been established.

[8] J. Saltiel, *Surv. Progr. Chem.*, 2, 286 (1964).

[9] W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Amer. Chem. Soc.*, 88, 2742 (1966).

[10] J. Saltiel, R. M. Coates, and W. G. Dauben, *ibid.*, 88, 2745 (1966).

[11] R. S. H. Liu and G. S. Hammond, *ibid.*, 86, 1892 (1964); 89, 4936 (1967).

1,3-pentadienes are planned as a possible test of this hypothesis.

Acknowledgment. This research was supported in part by the donors of the Petroleum Research Fund administered by the American Chemical Society, and by National Science Foundation Grant GP-7941.

---

[12] The analogous interpretation involving allylmethylene biradicals will also account for these observations.

[13] (a) Petroleum Research Fund Fellow; (b) Petroleum Research Fund Scholar.

Jack Saltiel, Lewis Metts,[13a] Mark Wrighton[13b]
Department of Chemistry, The Florida State University
Tallahassee, Florida 32306

Received March 4, 1970

Isoprene Triplets as Excitation Donors. Nonvertical Deexcitation

Sir:

The triplet states of conjugated dienes have aroused considerable interest in view of their intermediacy in sensitized isomerizations[1] and photodimerizations[2] of these systems. The pathways available to these species include isomerization of the double bonds, dimerization with a ground-state molecule, unimolecular decay, and quenching (presumably *via* triplet excitation transfer) by azulene.[2] Discussions of the structure of these triplets in fluid solution have been presented.[2-4] While it is clear that rotation about the 1,2 and 3,4 bonds is efficient with respect to the time required for decay[1] and that rotation about the 2,3 bond is restricted on that time scale,[2] it is not clear whether a freely rotating 1,4-biradical or an allylmethylene structure is the better structural representation.[3,4] Dienes are claimed to be "nonvertical" acceptors of triplet excitation,[2] but the situation with dienes as *donors* of triplet excitation has not been extensively explored. A claim[5] that excitation transfer from 2,4-hexadiene triplets to ground-state hexadiene molecules can be very efficient has been disproved.[3] The present results relate to this facet of diene triplet chemistry and permit the following conclusions: (1) excitation transfer from isoprene triplets occurs, albeit inefficiently, with the stilbene isomers, acceptors whose triplet energies are in the range of 50–57 kcal/mol,[1] and (2) the lowest observed spectroscopic triplet of isoprene at 60.1 kcal/mol[6] is not the excitation donor.

In the course of a previous study[7] it was observed that the presence of isoprene in a sample of 3,4-diphenylbutyrophenone undergoing Norrish II photofragmentation to acetophenone and stilbene caused changes in the *cis* to *trans* ratios of the stilbenes.[7b] Further exploration of this phenomenon *via* the isomerization of stilbenes photosensitized in the system, benzophenone–isoprene, indicated marked deviation from predictions based on the assumption that isoprene acts only as a quencher for benzophenone triplets. The mechanism, eq 1–10, allows derivation of expressions 11 and 12 for the *trans* to *cis* quantum yields and photostationary states, respectively; an obvious analog to eq 11 holds for $\phi_{c\rightarrow t}$.

$$(C_6H_5)_2C{=}O \xrightarrow{h\nu} \rightsquigarrow (C_6H_5)_2C{=}O^3\ (S^3) \tag{1}$$

$$S^3 + trans\text{-stilbene } (t\text{-S}) \xrightarrow{k_t} S + (\text{stilbene})^3\ (P^3) \tag{2}$$

$$S^3 + cis\text{-stilbene } (c\text{-S}) \xrightarrow{k_c} S + P^3 \tag{3}$$

$$S^3 + \text{isoprene (I)} \xrightarrow{k_I} S + I^3 \tag{4}$$

$$I^3 + t\text{-S} \xrightarrow{k_{t\text{-I}}} I + P^3 \tag{5}$$

$$I^3 + c\text{-S} \xrightarrow{k_{c\text{-I}}} I + P^3 \tag{6}$$

$$I^3 \xrightarrow{k_D} I \tag{7}$$

$$I^3 + I \xrightarrow{k_B} \text{dimers} \tag{8}$$

$$P^3 \xrightarrow{k_1} t\text{-S} \tag{9}$$

$$P^3 \xrightarrow{k_2} c\text{-S} \tag{10}$$

$$\frac{k_1 + k_2}{k_2}\phi_{t\rightarrow c} = \frac{k_t(t\text{-S})}{k_I(I) + k_t(t\text{-S})} + \frac{k_I(I)}{k_I(I) + k_t(t\text{-S})} \times \frac{k_{t\text{-I}}(t\text{-S})}{k_{t\text{-I}}(t\text{-S}) + k_D + k_B(I)} \tag{11}$$

$$\frac{k_2}{k_1} = \frac{(c\text{-S})|_{\text{pss}}}{(t\text{-S})|_{\text{pss}}} \times \frac{k_c + \dfrac{k_{c\text{-I}}k_I(I)}{k_{t\text{-I}}(t\text{-S})|_{\text{pss}} + k_{c\text{-I}}(c\text{-S})|_{\text{pss}} + k_D + k_B(I)}}{k_t + \dfrac{k_{t\text{-I}}k_I(I)}{k_{t\text{-I}}(t\text{-S})|_{\text{pss}} + k_{c\text{-I}}(c\text{-S})|_{\text{pss}} + k_D + k_B(I)}} \tag{12}$$

The presumption that $k_{t\text{-I}} = k_{c\text{-I}} = 0$ leads to several inconsistencies. First, and most telling, the photostationary states in all cases would be predicted to be 59 ± 0.5% *cis*.[1] In fact, the photostationary states we have observed are 79.6 ± 0.4% *cis* in 2–3 *M* isoprene and 83.7 ± 0.2% *cis* in neat (10 *M*) isoprene. It is clear that a process must be occurring which favors *cis*. Second, the reasonable presumption that $k_t = k_c = k_I$ = diffusion controlled allows estimation of the quantum yield of isomerization if S^3 but not I^3 can produce stilbene triplets. Those estimations are uniformly low for both $\phi_{t\rightarrow c}$ and $\phi_{c\rightarrow t}$. The effect is difficult to quantitate precisely for $\phi_{c\rightarrow t}$ for several technical reasons,[8] but Table I gives clear-cut evidence for $\phi_{t\rightarrow c}$. The effect could in principle have arisen from direct absorption of stray light into the stilbene; however, results are independent of benzophenone concentration over the range 0.06–0.27 *M*, and the direct absorption hypothesis would have predicted that benzophenone would have been an effective internal

---

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

[2] R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **87**, 3406 (1965).

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

[4] R. Hoffmann, *Tetrahedron*, **22**, 521 (1966).

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

[6] (a) D. F. Evans, *J. Chem. Soc.*, 1735 (1960); (b) R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

[7] (a) R. A. Caldwell and P. M. Fink, *Tetrahedron Lett.*, 2987 (1969); (b) P. M. Fink, Senior Honors Thesis, Cornell University, 1969. P. M. F. deserves credit for initially formulating the correct explanation of this phenomenon.

[8] Those reasons are: (1) the effect is much smaller for *cis*, requiring higher concentrations of isoprene for its observation. Under those conditions we have little guarantee that the rate constant for excitation transfer from benzophenone triplet to isoprene reflects a diffusional process: P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 90, 2232 (1968). (2) Since the photostationary state is quite *cis*-rich, back-reaction corrections (which in this case have no analytical solution) become important.