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

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(12) The analogous interpretation involving allylmethylene biradicals will also account for these observations.

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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 $\phi_{c\rightarrow t}$.

$$(\mathrm{C_6H_5})_2\mathrm{C{=}O} \xrightarrow{h\nu} \rightsquigarrow (\mathrm{C_6H_5})_2\mathrm{C{=}O}^3\ (\mathrm{S}^3) \tag{1}$$

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

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

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

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

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

$$\mathrm{I}^3 \xrightarrow{k_\mathrm{D}} \mathrm{I} \tag{7}$$

$$\mathrm{I}^3 + \mathrm{I} \xrightarrow{k_\mathrm{B}} \text{dimers} \tag{8}$$

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

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

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

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

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 $k_t = k_c = k_\mathrm{I}$ = 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

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(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).

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(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.

Table I. Photosensitized Isomerization of Stilbene with Benzophenone in the Presence of Isoprene

trans-Stilbene, M	Isoprene, M	ϕ_{obsd} (*trans*→*cis*)[a]	$\phi_{\text{predicted}}$
0.056	0	0.55^{b}	0.56^{d}
0.045	0.108	0.23_{1}^{c}	0.173^{e}
0.045	0.52	0.10_{6}^{c}	0.0475^{e}
0.045	1.05	0.084^{c}	0.0242^{e}
0.045	5.2	0.045_{4}^{c}	0.0050^{e}
0.022	3.0	0.025_{8}^{c}	0.0043^{e}

[a] Experiments were performed at 3660 A in benzene solvent. Gas chromatographic analyses were reproducible to ±3%. Conversion was roughly 4–6% in general and never over 12%. [b] Conventional ferrioxalate actinometry. [c] Actinometry *via* unquenched samples which were irradiated either in parallel or both before and after, corrected for back-reaction by the method of Hammond and Lamola (*J. Chem. Phys.*, **43**, 2129 (1965)). [d] H. A. Hammond, D. E. DeMeyer, and J. L. R. Williams, *J. Amer. Chem. Soc.*, **91**, 5180 (1969). [e] $\phi_{\text{predicted}} = 0.59 \times$ stilbene molarity/(stilbene molarty + isoprene molarity); $0.59 = k_2/(k_1 + k_2)$ from ref 1.

filter. The only apparent explanation is that *isoprene triplets must be capable of transferring excitation to the stilbenes.*[9] The magnitude of the effect is such that, at 1 M isoprene, about 12% of the isoprene triplets transfer excitation to 0.05 M *trans*-stilbene ($E_T = 50$) and about 3% transfer excitation to 0.05 M *cis*-stilbene ($E_T = 57$). It is not surprising that Saltiel's study[8] detected no excitation transfer with hexadiene.

For $k_c = k_t = k_I$ and $k_2 = 1.43k_1$,[1] we calculate that $k_D/k_{t\text{-}I} = 0.32 \pm 0.04$ M and $k_B/k_{t\text{-}I} = 0.06 \pm 0.02$ M, from the data in Table I. Our best estimates from comparable data starting with *cis* are *ca.* 2 ± 1 M for $k_D/k_{c\text{-}I}$ and 0.2 ± 0.1 for $k_B/k_{c\text{-}I}$. The $\phi_{t\to c}$ data indicate $k_D/k_B = 6 \pm 2$ M, in fair agreement with the value of 16 M obtained by Liu, Turro, and Hammond.[2] Quantitative comparison of our results and those for azulene quenching of isoprene triplets[2] ($k_{Az}/k_B = 1200$) indicate that *trans*-stilbene is much less efficient than azulene in quenching isoprene triplets. Despite the fact that the reaction is some 10 kcal/mol exothermic (based on the spectroscopic triplet energies), *trans*-stilbene quenches isoprene triplets *at least some two orders of magnitude less than diffusion controlled.*

The obvious explanation for the slowness of this rate, that isoprene triplets are nonvertical[1,2] and therefore not subject to expectations based on conventional triplet excitation donors, is surely right in general but does not probe the nature of this donor–acceptor interaction. Two reasonable possibilities come to mind: (1) excitation transfer is accomplished relatively efficiently from the small amount of spectroscopic triplet in thermal equilibrium with the remainder of the isoprene triplet molecules, or (2) deexcitation occurs from a nonvertical geometry. Our results indicate the latter explanation. The spectroscopically accessible isoprene triplet at 60 kcal should behave essentially like any other donor triplet of comparable energy in its k_t/k_c ratio, *i.e.*, the excitation ratio for the stilbene isomers. That ratio is 1.6 for several sensitizers of $E_T = 59.5 \pm 0.3$ kcal.[1] The quantum yield data given above indicate a rough value of ∼5 for isoprene triplets. A much more precise value of 4 ± 0.5 may be obtained by analysis of the photostationary state data *via* eq 12 and the parameters derived from eq 11. This ratio is clearly not characteristic of a 60-kcal triplet.

Adroit application of the techniques we describe should ultimately provide a wealth of revealing data on the nature of bimolecular deactivation of nonvertical triplets.

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[9] We rule out the possibility that the triplet isoprene–stilbene interaction responsible for isomerization is biradical in nature, since such a process would be expected to favor production of *trans*-stilbene rather than *cis*; *cf.* ref 7a, among other recent references to photochemically generated biradicals.

Chemiluminescence from the Reaction of Ketenes, Singlet Oxygen, and Fluorescers

Sir:

We find that reactions of certain ketenes and ketene acetals with singlet oxygen and fluorescers (Flr) produce chemiluminescent light emission. Bright light emission occurs when solutions of ketene or diphenylketene and triphenyl phosphite ozonide[1] in methylene chloride are mixed at −70° and allowed to warm to room temperature in the presence of 9,10-bis(phenylethynyl)anthracene (BPEA) or 9,10-diphenylanthracene (DPA). The reaction of diphenylketene glycol acetal produces a very weak light emission and tetraphenylethylene fails to react under these conditions.

The spectrum of chemiluminescent light emission from the diphenylketene reaction is identical with the fluorescence of BPEA, the fluorescer used. The chemiluminescent quantum yields were measured and are summarized in Table I. The quantum yield based on diphenylketene is 1.9×10^{-4} einstein mol^{-1} and decreases slightly with increasing concentration of diphenylketene. The quantum yield decreases more strongly with decreasing BPEA concentration. Although some of the fluorescer may react with singlet oxygen to form an *endo*-peroxide, a possible decomposition of that *endo*-peroxide is not responsible for the light emission since 9,10-diphenylanthracene *endo*-peroxide is stable under the reaction conditions.

Table I. Chemiluminescent Emission from the Reaction of Diphenylketene and Singlet Oxygen

Diphenylketene, $10^2 \times$ mol l.$^{-1}$	BPEA, mol l.$^{-1}$	Quantum yield, einstein mol^{-1} $\times 10^{-4}$
0.463	1×10^{-3} + 0.01 g of solid	1.92
1.7	1×10^{-3} + 0.01 g of solid	1.6
3.0	1×10^{-3} + 0.01 g of solid	1.3
6.0	1×10^{-3} + 0.01 g of solid	1.0
3.5	3×10^{-3}	1.1
6.2	3×10^{-3}	0.33
11.3	1×10^{-3} + 0.01 g of solid	1.0
13.1	1×10^{-3}	0.15
None	1×10^{-3} + 0.01 g of solid	≦0.001

Weak light emission is also observed from singlet oxygen and BPEA or DPA in the absence of ketene. The emission spectrum agrees well with the fluorescence of the BPEA used and the quantum yield is low, $\sim 1 \times 10^{-7}$ einstein mol^{-1} of $^1O_2$. An energy pooling

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[1] R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 537 (1968); **91**, 5358 (1969).