in the solid (~260 ppm) is certainly significantly larger than those observed in solution (~100 ppm).

Several of the compounds in Table II are of interest in relation to other studies. Cadmium *n*-butylxanthate and cadmium ethylxanthate may represent analogues to the cadmium protein systems (e.g., metallothionines) currently being studied in other laboratories.[9] The tetraalkylammonium halocadmates have been examined by Drakenberg et al. and by Maciel et al. in solution.[8,22]

^{113}Cd chemical shifts were also obtained on 0.1 M solutions of many of the compounds of Table II in H_2O and/or dimethyl sulfoxide. Almost invariably, and not surprisingly, the shifts obtained in solution are substantially different from the corresponding data obtained in the crystalline state. This simply reflects the complexity of the solution chemistry of these Cd(II) systems, and in many cases reflects the fact that the solution ^{113}Cd shifts are weighted averages of various species in rapid equilibria.[5-8,23] The shift values obtained for 0.1 M solutions are as follows (in ppm): cadmium perchlorate, −0.2 in H_2O and −27.0 in Me_2SO; cadmium formate, −10.3 in H_2O; cadmium sulfate, −1.7 in H_2O; cadmium maleate, −35.2 in Me_2SO; calcium cadmium acetate, −26.5 in H_2O and −12.3 in Me_2SO; cadmium(II) acetate, −20.1 in H_2O and −12.8 in Me_2SO; cadmium ammonium sulfate, −2.7 in H_2O; cadmium nitrate, −33.0 in H_2O and −34.8 in Me_2SO.

Conclusions

^{113}Cd chemical shifts, as well as shift anisotropies, can be obtained relatively conveniently on solid samples representing specific coordination details of interest. These data can provide unequivocal benchmark shift data that ordinarily cannot be obtained from solution experiments unless extensive studies of pertinent equilibria are also undertaken. This approach should be useful for several spin-$^{1}/_{2}$ metal nuclides.

Acknowledgment. We gratefully acknowledge support of this research by National Science Foundation Grant No. CHE74-23980 and use of the Colorado State University Regional NMR Center, funded by National Science Foundation Grant No. CHE 78-18581.

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Photosensitized Geometric Isomerization of Alloocimene. The Triplet Torsional Potential Surface of a Conjugated Triene[1]

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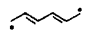
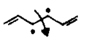
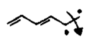
The photostationary state compositions and quantum yields of the benzophenone-sensitized geometric isomerization of alloocimene, a model triene, have been studied in detail. The results are discussed in terms of two reaction schemes for four isomer systems (one for steady-state concentrations of isomers and one for partially equilibrated isomeric triplets). A triplet torsional potential surface of the triene is also presented which was constructed to reflect the photochemical properties of the triene. From quenching data, the average lifetime of an alloocimene triplet at room temperature was determined to be 2 × 10^{-7} s.

Introduction

Conjugated trienes occupy a unique position in studies of photosensitized isomerization of conjugated polyenes. Previous studies from this laboratory showed that the photochemical properties of trienes are sensitive to structural modifications[2,3] which affect the relative stability of several possible excited intermediates (planar, diallyl,


planar


diallyl


methylenepentadienyl

and methylenepentadienyl) in the sensitized reaction. In this paper we discuss results of a study on the sensitized isomerization reaction of alloocimene, a model conjugated

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TABLE I: Photostationary State Compositions of Alloocimene in Benzophenone-Sensitized Reaction with Guaiazulene (G) or Azulene (A) as a Quencher, or without a Quencher[a]

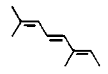
			percentage of isomers[c]				
quencher	10^{-3}[Q], M	[A],[b] M	tt	tc	ct	cc	cc/ct
G	20	0.04	47.7	54.3	trace	0.7	
	16	0.04	41.1	55.6	0.8	0.9	1.1
	12	0.04	41.2	56.8	0.9	1.1	1.2
	8.0	0.04	40.0	55.6	1.5	1.7	1.1
	4.0	0.04	40.2	55.0	2.2	2.8	1.3
	1.6	0.04	38.7	55.0	2.1	2.8	1.3
	0.8	0.04	40.3	36.6	7.7	10.0	1.3
	0.4	0.04	41.1	31.2	13.1	14.6	1.1
	0.1	0.04	39.9	28.8	14.5	16.8	1.2
	0.025	0.04	40.2	27.7	15.1	17.0	1.2
	0.0063	0.04	39.1	27.6	16.1	17.3	1.1
	0.0016	0.04	39.4	27.4	15.8	17.4	1.1
	0	0.04	40.5	27.2	15.0	17.4	1.2
A	4.0	0.04	39.2	54.7	2.5	3.6	1.4
	3.2	0.04	39.4	53.5	2.9	4.2	1.4
	1.6	0.04	40.5	48.3	4.7	6.6	1.4
	0.8	0.04	40.2	42.5	6.8	10.6	1.5
	0	0.21	54.8	30.1	7.2	7.9	1.1
		0.0512	42.9	26.2	14.4	16.5	1.1
		0.0256	36.2	25.2	18.5	20.6	1.1
		0.0125	34.6	25.7	18.5	21.2	1.2
		0[d]	29.4	25.0	20.8	25.3	1.2

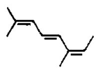
[a] [$Ph_2C=O$] = 0.1 M. [b] Concentration of alloocimene. [c] Estimated error limits = ±0.3. [d] Extrapolated values.

triene. In particular, the question of the relative stability of the above-mentioned intermediates in this system and how the chemistry is affected will be examined.

Results

The commercially available alloocimene contained primarily the two central trans isomers (tt, tc). They were


tt


tc


ct


cc

separated by preparative GLC. The two central cis isomers (ct, cc) were isolated from a photostationary state mixture after sensitized irradiation, again by preparative GLC, using conditions similar to those reported by Crowley.[4]

Photostationary State Measurements. The photostationary states of benzophenone-sensitized isomerization reaction were established without detectable amounts of dimers. Similar to the stilbenes,[5] the photostationary state composition of the triene was found sensitive to the presence of small amounts of a triplet quencher such as azulene or guaiazulene (1,4-dimethyl-7-isopropylazulene). The data are listed in Table I.

Quantum Yield Measurements. The quantum yields of benzophenone-sensitized isomerization of each of the four isomers of alloocimene to the other three isomers were determined (Table II). The conversion of reaction was kept low (an average of 8%); hence any corrections due to back-isomerization should be small, and therefore were not made. Benzophenone-sensitized isomerization of *trans*-stilbene was used as the actinometer system.[5] Analytical GLC was the method used for analyses.

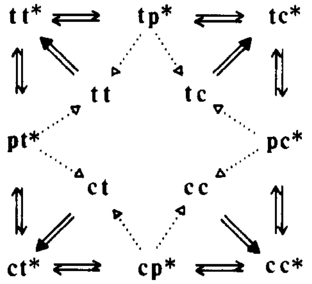
Discussion

TABLE II: Quantum Yields of Benzophenone-Photosensitized Isomerization of Isomers of Alloocimene[a]

			Φ of product isomer[b,c]			
run no.	starting isomer	concn, M	tt	tc	ct	cc
1	tt	0.04		0.369	0.120	0.135
2	tt	0.04		0.364	0.143	0.162
3	tt	0.06		0.505	0.171	0.199
1	tc	0.04	0.942		0.245	0.265
2	tc	0.04	0.943		0.245	0.281
3	tc	0.06	1.52		0.182	0.225
1	ct	0.04	0.209	0.166		0.265
1	cc	0.04	0.230	0.147	0.178	

[a] The solvent was hexane. [b] Average conversion = 8%. No attempt to correct possible back-isomerization.
[c] Standard deviation from the mean = ±0.009, based on runs 1 and 2.

Scheme I



Reaction Scheme for Four Isomer Systems. In our discussion of the photoisomerization process, we define a four isomer system as one containing four distinguishable geometric isomers. It includes alloocimene and any unsymmetrically substituted dienes (such as 2,4-heptadiene) and all other systems containing two unsymmetrically substituted double bonds whether they are part of a conjugated or unconjugated diene or triene system. For such systems one photon of light can lead to isomerization at one or both unsymmetrically double bonds. Examples of exclusive one-photon–one-bond isomerization are diphenyl-1,3-butadienes[6,7] and direct irradiation of hexatrienes.[8] Examples of one-photon–two-bond isomerization

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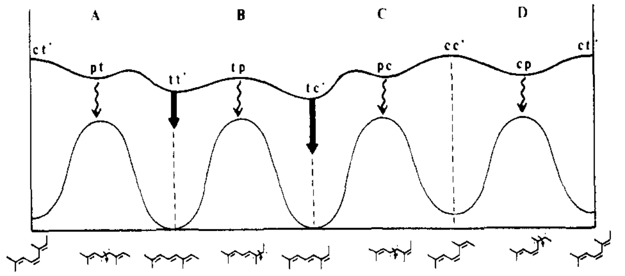

Figure 1. A two-dimensional potential surface of triplet (dark line) and ground-state (light line) alloocimene dissected into (A) the ct $\rightleftarrows$ tt curve, (B) the tt $\rightleftarrows$ tc curve, (C) the tc $\rightleftarrows$ cc curve, and (D) the cc $\rightleftarrows$ ct curve. Wavy lines indicate radiationless decay processes in the absence of azulene; the heavy arrow lines, the azulene quenching processes. Since the two end lines are identical, the diagram represents a continuous two-dimensonal potential curve.

are sensitized isomerization of 2,4-hexadiene,[9] conjugated trienes,[8] and several dienones.[10] Here, we would first like to consider a general scheme that takes into consideration both of these situations.

The flow diagram for the photoisomerization reaction of a four isomer system is depicted in Scheme I. The four isomers are designed as tt, tc, ct, and cc. Their planar excited counterparts are labeled with an additional asterisk. Any orthogonal species as a result of rotation of a double bond is indicated by replacement of c or t by p. The double lines represent excitation, single lines, interconversion of excited species and dashed lines, deactivation processes.

The one-photon–one-bond and one-photon–two-bond processes represent two extreme cases of the flow chart in Scheme I. When interconversions of excited-state species are slow with respect to rates of decay of intermediates, only one-bond isomerization can take place. When interconversions of excited-state species are rapid with respect to the decay rates then two-bond isomerization will accompany one-bond isomerization. Furthermore, complete equilibration of excited intermediates immediately implies that the photochemistry will become independent of the nature of the starting isomer.

Qualitative Aspects of the Triplet Torsional Potential Surface of Alloocimene. From the results of initial product distribution and quenching effect on photostationary state compositions, it is possible to construct a qualitative torsional potential surface of triplet alloocimene. We shall discuss the surface in terms of the four potential curves along the edges of the flow diagram involving twisting the two double bonds capable of undergoing geometric isomerization. The curves are sketched continuously in Figure 1. The ct $\rightleftarrows$ tt curve should take the form very similar to that of stilbene in that tt* is much more stable than the sterically crowded ct*. Upon excitation of either isomer, the triplet relaxes into a well tt* which is in equilibrium with the intermediate diallyl structure (pt*). Radiationless decay takes place at pt* giving either ct or tt; but quenching originates only from tt* giving exclusively tt. Along the tt $\rightleftarrows$ tc curve since quenching appears to take place from both tt* and tc*, the two species must be very close in energy. The decay ratio (the *n* value, see below), however, indicates a perference for formation of the tc isomer suggesting that tc* is slightly more stable than tt*. Whether the two species should be connected by a low barrier or a shallow well is not so obvious. We perfer the former because it appears that the isomerization is an activated process. Isomerization about this bond becomes a consequence of interconversion of planar triplets. The tc $\rightleftarrows$ cc curve is close to the mirror image of that of ct $\rightleftarrows$ tt. Again, because of steric interaction, the planar cc* triplet should be unstable, while the planar tc* structure more stable. Similarly, isomerization takes place at the intermediate pc* structure while quenching takes place at the planar tc*. Along the cc $\rightleftarrows$ ct curve, both planar structures are unstable relative to the neighboring pc*, pt* structures. As to the question whether the planar cc* and ct* species should be connected by a barrier or a well, we believe the latter is correct because, only with a well, can isomerization at the central bond be competitive with reaction at the terminal bond as shown in Table I. Incidentally, on steric ground one would also reason that cp* should be more stable than the planar species. (In drawing Figure 1 we have, in fact, assumed on steric ground that all perpendicular species are approximately the same in energy.)

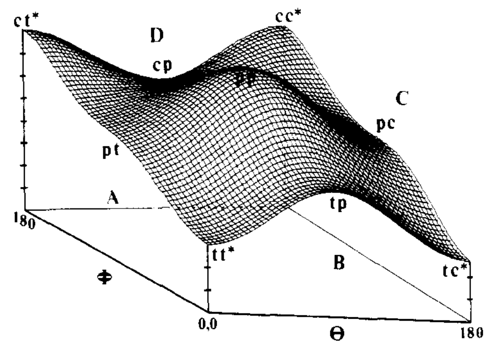

Figure 2. A hypothetical torsional potential surface for triplet alloocimene. The four edges of the surface were constructed by using equations of the form of either $a \cos \Phi + b \cos 3\Phi$ (curves A and C) or $c \cos 2\theta$ (curves B and D). In joining the opposite curves, an additional hyperbolic function of the form $de^{-(\Phi-90)^2}de^{-(\theta-90)^2}$ was added. The approximate relative heights of different species are tc* = 0, tt* = 0.7, ct* = cc* = 6, pt = tp = pc = cp = 3 kcal/mol. The summit in the middle of the plot (pp) has been assigned arbitrarily with a relative height of 12 kcal/mol.

The approximate relative heights of the excited-state species are estimated in the following way. The heavy atom enhanced (methyl iodide) $S_0 \rightarrow T_1$ absorption measurement was carried out only with a mixture of the two central trans isomers of alloocimene. The observed value (46.9 kcal/mol) is almost identical with the 47 kcal/mol value reported for *trans*-1,3,5-hexatriene.[11] That azulene (E_T = 39 kcal/mol)[12] and guaiazulene (presumably a lower E_T) gave identical quenching results also suggests that the E_T of alloocimene is above 40 kcal/mol so that transfers to quenchers are equally efficient. Based on the decay ratio, one may assume that tt* is only approximately 1 kcal/mol higher than that of tc*. On the other hand, ct* and cc* must be at least another 4 kcal/mol higher. The central cis isomers, based on heats of hydrogenation measurements, were estimated to be 4.7 kcal/mol higher in energy than the central trans.[13] This would suggest that the corresponding triplet excitation energy for the central cis isomers should be close to that of the central trans isomers. In the hexatriene case the excitation energy of

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(11) Minnaard N. G. Ph.D. Dissertation, University of Leiden, 1970; also Jacobs, H. J. C.; Havinga, E. *Adv. Photochem.* **1978**, *11*, 305–73.

(12) Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161–7.

(13) The 4.7 kcal/mol was the difference in heats of hydrogenation for the two isomers of 2-methyl-1,3,5-hexatriene determined at Rice University (private communication of Professor R. B. Turner). For heats of hydrogenation of other trienes see: Turner, R. B.; Mallon, B. J.; Tichy, M.; Doering, W. von E.; Roth, W. R.; Schröder, G. *J. Am. Chem. Soc.* **1973**, *95*, 8605–10.

Scheme II

excitation

$$S \xrightarrow{h\nu} S^1 \rightarrow S^3$$

$$S^3 + tt \overset{k_1}{\Rightarrow} S + X$$

$$S^3 + tc \overset{k_2}{\Rightarrow} S + X$$

$$S^3 + tc \overset{k_3}{\Rightarrow} S + X$$

$$S^3 + cc \overset{k_4}{\Rightarrow} S + X$$

decay

$$X \overset{k_5}{\dashrightarrow} tt$$

$$X \overset{k_6}{\dashrightarrow} tc$$

$$X \overset{k_7}{\dashrightarrow} ct$$

$$X \overset{k_8}{\dashrightarrow} cc$$

self-quenching

$$X + AO \xrightarrow{k_9} m\,tt + (1 - m)tc + AO$$

quenching

$$X + Q \xrightarrow{k_q} n\,tt + (1 - n)tc + Q$$

the central cis isomer is in fact only 1 kcal/mol higher than that of the trans.[11] This analysis is also consistent with the result that the photostationary state mixture of alloocimene is not very sensitive to variation of energy of the sensitizer employed.[14]

When all the essential features (relative positions of hills and valleys) of the torsional curves are combined, the continuous potential curve in Figure 1 is obtained. Because the end lines are identical, the figure represents a two-dimensional potential surface.

To describe the torsional potential surface of the triplet alloocimene more clearly, we have constructed in Figure 2 a three-dimensional diagram, entirely based on the chemistry discussed above. The four edges of the potential surface represent the four torsional potential curves in Figure 1. In joining the lines across the potential curves, we have (dictated by the chemical evidence of the absence of a common intermediate) introduced a barrier at the center of the surface. The chemistry therefore takes place along the edges of the surface.[15] A similar surface for a one-bond isomerization system has been presented elsewhere.[7]

Some Quantitative Aspects of the Alloocimene Triplets. The triplet-state isomerization reaction of alloocimene represents an intermediate case between the two extremes. Data in Table I clearly show that starting with any of the four isomers, two-bond isomerization (e.g., tt to cc) accompanies one-bond isomerization (tt to tc or ct). On the other hand, a closer examination of the data also shows that equilibration of all excited intermediates was not complete within the lifetime of the excited species. For example, the quantum yields from tt to ct and tc are not the same as the corresponding values from cc to the same two isomers.

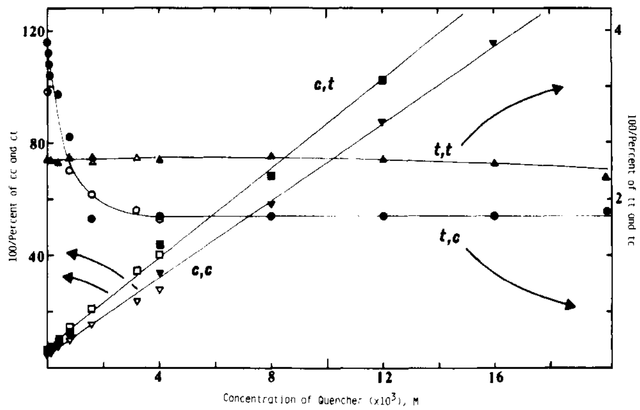

Figure 3. Photostationary state composition of alloocimene isomers as a function of concentration of azulene. The left vertical scale is for c,c (▼) and c,t (■) and the right scale for t,t (▲) and t,c (●) isomers. The filled-in points are those obtained with guaiazulene as quencher and the unfilled ones are those with azulene as quencher. The intercepts of the c,c and c,t lines are 5.2 and 6.5 and the corresponding slopes are 6.8 and 8.2 × 10^3.

The kinetic expressions for the quantum yields of isomerization of such a nonequilibrated system are quite complicated (see the section below). However, the kinetic expressions for photostationary state values are much simpler because one can now assume that the steady states generated by prolonged irradiation are kinetically equivalent to that of fully equilibrated excited intermediates. The minimum number of steps to describe this situation, after including bimolecular quenching are shown in Scheme II.

Most of the symbols are self-explanatory. The constants m and n are used to designate partitioning of triplets to the two central trans isomers in respectively the self-quenching and the azulene quenching steps. The first eight steps as well as the excitation steps are essentially those in the flow scheme. The last two steps are now added because of the observed dependence of photostationary states on azulene (quencher, Q) or trienes (AO) concentrations.

Based on this scheme and using usual steady-state assumptions, one obtains the following Stern–Volmer expressions governing the proportion of each isomer at photostationary states:

$$\left(\frac{100}{\%\mathrm{tt}}\right)_s = \frac{1/\tau + k_9[\mathrm{AO}] + k_q[\mathrm{Q}]}{k_5 + mk_9[\mathrm{AO}] + nk_q[\mathrm{Q}]}$$

$$\left(\frac{100}{\%\mathrm{tc}}\right)_s = \frac{1/\tau + k_9[\mathrm{AO}] + k_q[\mathrm{Q}]}{k_6 + (1 - m)k_9[\mathrm{AO}] + (1 - n)k_q[\mathrm{Q}]}$$

$$\left(\frac{100}{\%\mathrm{ct}}\right)_s = \frac{1/\tau}{k_7} + \frac{k_9[\mathrm{AO}]}{k_7} + \frac{k_q[\mathrm{Q}]}{k_7}$$

$$\left(\frac{100}{\%\mathrm{cc}}\right)_s = \frac{1/\tau}{k_8} + \frac{k_9[\mathrm{AO}]}{k_8} + \frac{k_q[\mathrm{Q}]}{k_8}$$

where $\tau = (k_5 + k_6 + k_7 + k_8)^{-1}$.

These expressions allow experimental tests of the correctness of the scheme shown above. They predict that the reciprocal of the concentration of the two, and only, central cis isomers are linearly dependent on the concentration of quencher when a constant concentration of triene is used, and linearly dependent on the concentration of

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[14] Ramamurthy, V.; Butt, Y.; Yang, C.; Yang, P.; Liu, R. S. H. *J. Org. Chem.* **1973**, *38*, 1247–9.

[15] We wish to emphasize that Figure 2 is merely a graphic representation of the postulated triplet potential surface of alloocimene. It should be viewed as a visual aid to reflect qualitatively the relative positions of the planar and perpendicular species. The figure is obviously a simplified one omitting decay processes involving twisting of the symmetrically substituted double bond. Nevertheless, it is qualitatively meaningful. We hope it will stimulate interest among theoretical chemists to generate quantitatively meaningful potential surfaces for triplet trienes. The procedure to obtain such a plot was described in ref 7.

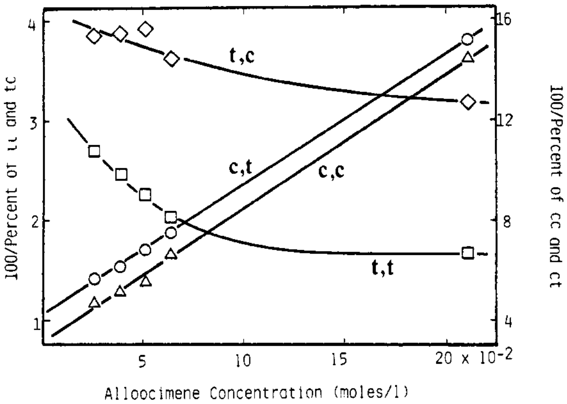

Figure 4. Photostationary state composition of alloocimene isomers as a function of concentration of triene. The left vertical scale is for t,t (□) and t,c (◇) isomers and the right scale for c,t (○) and c,c (△) isomers.

triene when no quencher is present. The data in Table II are plotted accordingly (Figures 3 and 4). The two quenchers appear to give identical results suggesting the rates of transfer of alloocimene triplets to both quenchers are identical and must be equal to diffusion-controlled rates. The predicted dependence of inverse of isomer concentrations on quencher or triene concentration is amply verified (tt being insensitive to quencher concentration).

From the slope and intercept of either line for cc or ct in Figure 3, the $k_q\tau$ value is calculated identically to be 1.3 $\times 10^3$ M^{-1}. If one assumes $k_q = k_{\text{diff}} = 6 \times 10^9$ M^{-1} s^{-1},[16] τ, the average lifetime of alloocimene triplets, is 2×10^{-7} s, which agrees with the observations made in kinetic flash photolysis experiments.[17] From Figure 4, the average value of k_9 is calculated to be 5×10^7 M^{-1} s^{-1}. The individual unimolecular decay constants are obtained from the slopes of the lines in Figure 3 and extrapolated zero concentration photostationary state values; k_5, k_6, k_7, and k_8 are respectively 10×10^5, 8.8×10^5, 7.3×10^5, and 8.8×10^5 s^{-1}. The partition coefficients m and n are respectively 0.59 and 0.38 (their significance has been discussed in the previous section).

A further test for the scheme is the ratio $([\mathrm{cc}]/[\mathrm{ct}])_s$ which is predicted to be a constant, equal to $k_8/k_7 = 1.2$. Data in Table I (last column) show that, throughout the quencher and triene concentration ranges, the ratio of %cc/%ct remains close to the predicted value.

A More General Scheme for a Four Isomer System. Although the above simplified scheme does serve a useful purpose for calculating the average lifetime of the alloocimene triplets, it does not describe the exact situation of the sensitized isomerization. Scheme III is a general scheme that contains the minimum number of steps to account for a situation involving nonequilibrated triplets. The scheme details the steps shown in the flow diagram in Scheme I. It assumes that radiationless deactivation (hence, the geometric isomerization reaction) can take place only from the perpendicular species. And, there is no direct interconversion between perpendicular species. Their interconversion takes place by way of the planar species (e.g., tp* → tc* → pc*). Any bimolecular processes are omitted here.

For a one-photon–one-bond isomerization process such as tt to tc, there is the primary route of tt* → tp* → tc and secondary routes of tt* → tp* → tc* → pc* → tc and tt* → tp* → tc* → tp* → tc. If we omit other higher order routes, for the sake of simplicity, we obtain the following quantum yield expression for the isomerization process:

$$\Phi_{\mathrm{tt}\to\mathrm{tc}} = \alpha(1-\alpha'')\frac{k_{19}}{k_{15}+k_{19}} + \alpha(1-\alpha')\frac{k_{15}}{k_{15}+k_{19}}\left[(1-\beta)(1-\alpha'')\frac{k_{19}}{k_{15}+k_{19}} + \beta\delta''\frac{k_{22}}{k_{18}+k_{22}}\right]$$

The quantum yield expression for the cc → tc process, again including those of the primary (cc* → pc* → tc) and secondary (cc* → pc* → tc* → tp* → tc and cc* → pc* → tc* → pc* → tc) routes only is

$$\Phi_{\mathrm{cc}\to\mathrm{tc}} = \delta''(1-\delta)\frac{k_{22}}{k_{18}+k_{22}} + (1-\delta)(1-\delta')\frac{k_{18}}{k_{18}+k_{22}}\left[(1-\beta)(1-\alpha'')\frac{k_{19}}{k_{15}+k_{19}} + \beta\delta''\frac{k_{22}}{k_{18}+k_{22}}\right]$$

On the other hand, the quantum yield expression for a two-bond isomerization process contains only secondary (or higher order) routes. That for tt to cc becomes (after omitting higher order routes)

$$\Phi_{\mathrm{tt}\to\mathrm{cc}} = \alpha(1-\alpha')\beta(1-\delta'')\frac{k_{15}}{k_{15}+k_{19}}\,\frac{k_{22}}{k_{18}+k_{22}} + (1-\alpha)(1-\beta')(1-\gamma)(1-\gamma'')\frac{k_{16}}{k_{16}+k_{20}}\,\frac{k_{21}}{k_{17}+k_{21}}$$

Scheme III

excitation

$$\mathrm{S}^3 + \mathrm{tt} \Rightarrow \mathrm{S} + \mathrm{tt}^*$$

$$\mathrm{S}^3 + \mathrm{tc} \Rightarrow \mathrm{S} + \mathrm{tc}^*$$

$$\mathrm{S}^3 + \mathrm{ct} \Rightarrow \mathrm{S} + \mathrm{ct}^*$$

$$\mathrm{S}^3 + \mathrm{cc} \Rightarrow \mathrm{S} + \mathrm{cc}^*$$

planar to perpendicular triplets

$$\mathrm{tt}^* \xrightarrow{k_{11}} \alpha\mathrm{tp}^* + (1-\alpha)\mathrm{pt}^*$$

$$\mathrm{tc}^* \xrightarrow{k_{12}} \beta\mathrm{pc}^* + (1-\beta)\mathrm{tp}^*$$

$$\mathrm{ct}^* \xrightarrow{k_{13}} \gamma\mathrm{pt}^* + (1-\gamma)\mathrm{cp}^*$$

$$\mathrm{cc}^* \xrightarrow{k_{14}} \delta\,\mathrm{cp}^* + (1-\delta)\mathrm{pc}^*$$

perpendicular to planar triplets

$$\mathrm{tp}^* \xrightarrow{k_{15}} \alpha'\mathrm{tt}^* + (1-\alpha')\mathrm{tc}^*$$

$$\mathrm{pt}^* \xrightarrow{k_{16}} \beta'\mathrm{tt}^* + (1-\beta')\mathrm{ct}^*$$

$$\mathrm{cp}^* \xrightarrow{k_{17}} \gamma'\mathrm{ct}^* + (1-\gamma')\mathrm{cc}^*$$

$$\mathrm{pc}^* \xrightarrow{k_{18}} \delta'\mathrm{cc}^* + (1-\delta')\mathrm{tc}^*$$

deactivation

$$\mathrm{tp}^* \overset{k_{19}}{\dashrightarrow} \alpha''\mathrm{tt} + (1-\alpha'')\mathrm{tc}$$

$$\mathrm{pt}^* \overset{k_{20}}{\dashrightarrow} \beta''\mathrm{tt} + (1-\beta'')\mathrm{ct}$$

$$\mathrm{cp}^* \overset{k_{21}}{\dashrightarrow} \gamma''\mathrm{ct} + (1-\gamma'')\mathrm{cc}$$

$$\mathrm{pc}^* \overset{k_{22}}{\dashrightarrow} \delta''\mathrm{tc} + (1-\delta'')\mathrm{cc}$$

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(16) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769–77.

(17) Liu, R. S. H.; Butt, Y.; Herkstroeter, W. G. *Chem. Commun.* **1973**, 799–801.

With these expressions, we shall consider the two extreme cases involving equilibration of excited species. First, for systems where decay of perpendicular species is much faster than equilibration of isomeric triplets (i.e., k_{19}–$k_{22} >> k_{15}$–k_{18}), which is the condition for exclusive one-photon–one-bond isomerization the first two expressions are greatly simplified, now containing only the first term. In fact quantum yield of isomerization becomes a function of the partition coefficients only:

$$\Phi_{tt\rightarrow tc} = \alpha(1 - \alpha'') \qquad \Phi_{cc\rightarrow tc} = \delta''(1 - \delta)$$

Therefore, aside from accidental equivalence, there is no reason to expect that the two different isomers will have identical quantum yield of isomerization to an identical product. It is also obvious from the third expression that, under these circumstances, one-photon–two-bond isomerization is of no importance.

The other extreme case is that rates of equilibration of isomeric triplets are much faster than decay of the perpendicular triplets, i.e., k_{15}–$k_{18} >> k_{19}$–k_{22}. The second term in both of the one-bond isomerization process now becomes the dominant term:

$$\Phi_{tt\rightarrow tc} = \alpha(1 - \alpha')\left[(1 - \beta)(1 - \alpha'')\frac{k_{19}}{k_{15}} + \beta\delta''\frac{k_{22}}{k_{18}}\right]$$

$$\Phi_{cc\rightarrow tc} = (1 - \delta)(1 - \delta')\left[(1 - \beta)(1 - \alpha'')\frac{k_{19}}{k_{15}} + \beta\delta''\frac{k_{22}}{k_{18}}\right]$$

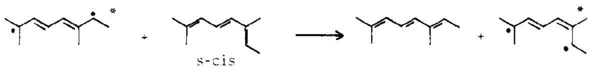
With the exception of the partition coefficients in the front they are identical.

In reality the omission of higher order routes (i.e., involving hopping more than once among perpendicular triplets), though successful in greatly simplifying the expression, does not agree with the imposed conditions for this extreme case. Rapid equilibration of triplets demands that the higher order terms be the dominant ones. Upon reflection it should be clear that each conversion from one perpendicular triplet to another will introduce two partition coefficients in front of the bracket. After completing a full cycle in interconversion of triplets the coefficients in the two quantum yield expressions for $\Phi_{tt\rightarrow tc}$ and $\Phi_{cc\rightarrow tc}$ should be the same making the two expressions identical. In other words quantum yields of product formation no longer have the memory of the nature of the reactant whether the net conversion is one of the above two one-bond isomerizations or a two-bond isomerization (e.g., $\Phi_{tc\rightarrow ct}$).

The alloocimene falls in between these two extremities. There are two bond isomerization (Table I) and yet quantum yields of product formation of any one isomer differ depending on the nature of the starting intermediates. In this sense the expressions shown above which include only the primary and secondary routes are probably reasonably accurate in representing the actual situation of competitive decay and interconversion of isomeric triplets. The decay processes (intersystem crossing) are not expected to be temperature dependent[18] while interconversion of triplets should. It will be of great interest to determine the quantum yield data at different temperatures. It should be pointed out that the temperature-dependent two-bond or one-bond isomerization ratio in 2,4-hexadiene is closely related to the current discussion of the trienes.[9]

Thermodynamic Vs. Kinetic Control in Relaxation of Triene Triplets. The discussion so far emphasizes the view that relaxation of Franck–Condon triplets are thermodynamically controlled, i.e., the partition coefficients are determined by the relative stability of the perpendicular triplets. It will be instructive to compare with some recent calculated results. Ab initio calculations show that methylenepentadienyl intermediates are more stable than diallyl intermediates,[19] thus in agreement with the data in Table I. (MINDO-III calculations led to the opposite conclusion.[20]) Since the planar species are calculated to be higher in energy than the perpendicular ones, interconversion of the latter will be activated. However, not taken into consideration in the calculations nor in the discussions so far are the kinetic parameters. It is highly probable that the direction of twisting of a planar triene triplet is kinetically controlled by factors such as differences in excited-state bond orders. Such a factor may be revealed in a temperature-dependent one-bond isomerization process. Another factor that can affect the photochemistry of trienes, particularly in cases of rapid equilibration of isomeric triplets, is the difference in relative ease of decay back to the ground state[8] which has to be taken into consideration in future experiments.

The Quantum Chain Process. The triene concentration effect appears to be characteristic of the trienes (also observed in hexatriene and 2,6-dimethyl-1,3,5-heptatriene[21] and bis(cyclopentyl)ethylene[3]), making it different from the otherwise very similar stilbene system. A quantum chain process is probably involved. While the exact nature of the quantum chain process is not known, a plausible one is represented by the following equation:



Unlike the excitation step when only the high-energy benzophenone triplets are the donors making the omission of the cisoid trienes reasonable, involvement of isomeric triplets does not become negligible for secondary processes. Some of the indirect evidence in support of this explanation are the following. (1) Although there is no direct evidence in the literature that the s-cis conformer of trienes is lower in energy than the s-trans conformer, this effect is well-documented in the diene series.[22,23] (2) In the vitamin D series where cisoid triene is not expected to exist, the triene concentration effect was not observed.[3] (3) In the simple trienes, 1,3,5-hexatriene and 2,6-dimethyl-1,3,5-heptatriene, where the s-cis conformers are expected to be present in larger equilibrium concentrations, larger concentration effects were observed.[21] (4) The stilbenes which do not have distinguishable s-cis and s-trans conformers do not exhibit concentration effect in the sensitized isomerization reaction.[5] It is, however, possible that such a secondary energy-transfer process was accompanied by another totally different process, namely, reversible formation of dimer diradicals. It is known that at high concentrations stable dimers are formed during triplet-sensitized irradiation of 1,3,5-hexatriene or 2,6-dimethyl-1,3,5-heptatriene.[24] This mechanism, however,

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(18) See, e.g., Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: New York, 1978: p 190.

(19) Bonacic-Koutecky, V.; Ishimaru, S. *J. Am. Chem. Soc.* **1977**, *99*, 8134–40.

(20) Ohmine, I.; Morokuma, K. *J. Chem. Phys.* **1980**, *73*, 1907–17.

(21) Butt, Y. Ph.D. Thesis, University of Hawaii, 1972.

(22) Liu, R. S. H.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1965**, *87*, 3406–12.

(23) Saltiel, J.; Metts, L.; Sykes, A.; Wrighton, M. *J. Am. Chem. Soc.* **1971**, *93*, 5302–3.

(24) Unpublished results of Pahk, M.; Arslanian, S.; Liu, R. S. H.

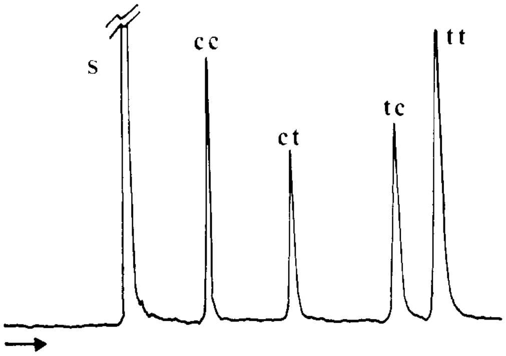

Figure 5. A representative chromatogram of the four isomers of alloocimene in hexane (S), obtained on a 200-ft TCEP capillary column, column temperature 75 °C. Approximate analysis time was 30 min.

can only increase the quantum yield of isomerization to a small extent.

Experimental Section

Materials. Alloocimene as a mixture of two central trans isomers was obtained from Chem Sample. It was distilled before use. The central cis isomers were generated by irradiating a dilute *n*-hexane solution of the commercial alloocimene in the presence of benzophenone. All the isomers were isolated by preparative GLC. The two central trans (tt, tc) isomers were separated on a 25 ft × $^3/_8$ in. column packed with 20% Carbowax 20M on Chromosorb W (80/100). The central cis isomers, cc and ct, were separated on a 20 ft × $^1/_4$ in. column containing 15% TCEP on Supelcoport (80/100). All the four isomers could also be separated in one step by using a binary phase column (15 ft × $^1/_8$ in.) made of 10% TCEP (2 parts) and 30% Carbowax 20M (1 part) on Chromosorb W (60/80). Benzophenone (Eastman) and *trans*-stilbene (Aldrich, gold label) were recrystallized from ethanol. Azulene and guaiazulene (Aldrich) were used as supplied. Solvents used in the irradiation were purified in the usual way.[7]

Irradiation Procedure. All irradiation samples were prepared, degassed, and sealed in the usual manner.[22] The light source for all photostationary and quantum yield studies was a 450-W Hanovia medium-pressure Hg lamp with Corning O-52 and 7-60 filter plates giving the 366-nm band. All samples were irradiated in parallel in the "merry-go-round" apparatus[25] at 23 °C. For quantum yield measurements, time of irradiation was adjusted so that conversion was approximately 8%. The benzophenone-sensitized trans-to-cis isomerization of stilbene was used as an actinometer. All the actinometer solutions were 0.01 M in *trans*-stilbene and 0.05 M in benzophenone. Photostationary state compositions were recorded only after two consecutive aliquots taken at an interval of 30 min gave identical composition values.

Analytical Procedure. Determination of *trans*- to *cis*-stilbene ratio in actinometer samples was performed by VPC analysis using a 3 ft × $^1/_8$ in. column made of 5% Apiezon M on Chromosorb W, 60/80 (column temperature, 150 °C). Alloocimene samples were analyzed by VPC, using either a 200-ft TCEP capillary column on a P.E. F-11 (column temperature, 75 °C) or a 20 ft × $^1/_8$ in. column packed with 10% TCEP on Supelcoport, 80/100 (column temperature, 100 °C), on a Varian 2800 unit, both equipped with a flame ionization detector (see Figure 5 for a sample chromatogram). For monitoring any possible loss of material during the irradiation period, an internal standard (toluene or benzene) was added to the irradiation samples. No significant amount of loss was observed. No corrections were found necessary for possible different isomer response on the flame ionization detector.

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[25] Moses, G. D.; Liu, R. S. H.; Monroe, B. *Mol. Photochem.* **1969**, *1*, 245–9.