able to the conformational rigidity of the units III derived from styrene, inserted into the copolymer macromolecules.

The above conformational rigidity should derive from the fact that unit III is incorporated into isotactic blocks of units IV which have been reported to have a helical conformation with one prevailing screw sense.[18]

The reported results indicate that the insertion of units III derived from styrene into the chains of optically active poly-α-olefins can function as an electronic probe[19] for exploring macromolecular conformation in the vicinity of the chromophore.

(18) P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Montagnoli, *Makromol. Chem.*, **61**, 207 (1963).

(19) The incorporation of aromatic compounds in polymers to investigate macromolecular conformations is known in protein chemistry (H. Morawetz, "Macromolecules in Solution," Interscience Publishers, New York, N. Y., 1965, pp 219–221, and references cited therein).

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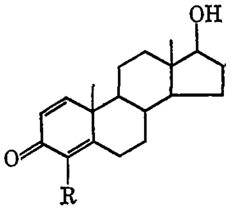
Efficiencies of Quenching of Short-Lived Excited Triplet States of Ketones with Dienes[1,2]

Sir:

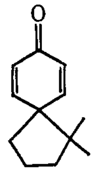
Recently, two of us reported that the reactive triplet excited state of α-santonin (I) was quenched much more efficiently by 1,3-cyclohexadiene than by piperylene.[3] We have now found that this effect is general for a series of 2,5-cyclohexadienones and also with a bicyclo[3.2.0]hept-6-en-2-one (V). The results are given in Table I as slopes of linear Stern–Volmer quenching plots using 1,3-cyclohexadiene ($k_q\tau_0$) and *trans*-piperylene ($k'_q\tau_0$) as triplet quenchers. Triplet energies of the ketones are given where known from phosphorescence emission, or determined with a graded series of sensitizers and quenchers. Also included are some quenching results for dimerization of cyclopentenone.[4]

With α-santonin, it was shown that, at the high concentration limit, quenching with 1,3-cyclohexadiene was due only (95–98%) to triplet-energy transfer,[3] according to the quantum yield of cyclohexadiene dimers.[5] These dimers[5] were noted in all runs using cyclohexadiene. Where adducts of quencher and ketone were indicated from glpc analysis by a reaction concomitant with energy transfer, the former process was always of much less importance.

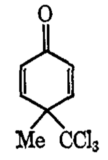
It is generally assumed that triplet-energy transfer in solution occurs at a diffusion-controlled rate as long as the triplet energy of the donor is greater than that of the acceptor by at least 3 kcal/mol.[6] Accordingly, energy transfer to 1,3-cyclohexadiene (E_T = 54 kcal)[7,8] and *trans*-piperylene (E_T = 59–60 kcal)[8] ought to be equally efficient for most, if not all, of the ketones in Table I.[9] It is particularly remarkable that the relative efficiencies of energy transfer to the two dienes, given as k_q/k'_q, increase as the absolute efficiencies given by the Stern–Volmer slopes decrease. It is clearly not warranted to make the assumption that energy transfer to either diene is occurring at the diffusion-controlled rate.[10] All piperylene plots are linear up to very high concentrations of diene, but upward curvature[10] is beyond experimental error on cyclohexadiene quenching (>4 *M*) of α-santonin and II, R = Me. It is not possible to extract from the data values of either k_q or τ_0 and hence of any rate constants for specific processes. It is likely that the triplet lifetime, τ_0, is increasing, although perhaps not monotonously, as one proceeds down the table.



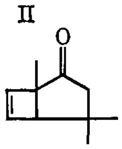
II



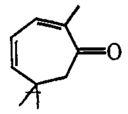
III



IV



V



VI

Differential quenching cannot be solely an effect of short triplet lifetimes, since the effect is not observed (within an experimental error of about 10%) with cyclopentenone whose lifetime is similar to those of other ketones in Table I.[4,11–13] Whether or not photodimerization occurs from T_1 or T_2, τ_0 is a function of cyclopentenone concentration, which was varied by a factor of 50 without observation of significant differential quenching.[13]

The results can be understood in the model framework for triplet-energy transfer proposed by Wagner.[10] Using his terminology[10] we assume that $k_{dif} = k'_{dif}$ and that $k_{-dif} = k'_{-dif}$,[14] but that $k_{et} \neq k'_{et}$, where k refers

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(1) Part XVIII of a series on the photochemistry of unsaturated ketones in solution. Part XVII: D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, in press.

(2) Research supported by grants from the U. S. Army Research Office, Durham (Project 4019-C), and the National Science Foundation (GP 7433).

(3) D. I. Schuster and A. C. Fabian, *Tetrahedron Letters*, 1301 (1968).

(4) P. E. Eaton and W. S. Hurt, *J. Am. Chem. Soc.*, **88**, 5038 (1966).

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

(6) (a) For an extensive review of triplet energy transfer, see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968). (b) See also N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 116 ff, and J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., 1966, p 348 ff, and references cited therein.

(7) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(8) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964); R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

(9) It is recognized that emission spectroscopy alone may not give accurate values for E_T, and that relaxed lower energy nonemitting triplets may be involved,[6a] although there is no evidence at present in support of this suggestion. However, with the low-energy triplets of eucarvone (E_T = 60 ± 1 kcal) and cyclopentenone (E_T = 61 kcal), differential quenching is *not* observed.

(10) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5715 (1967); P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).

(11) P. de Mayo, J. P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967).

(12) J. L. Ruhlen and P. A. Leermakers, *ibid.*, **89**, 4944 (1967).

(13) Assuming that k_q in benzene = 5×10^9 l. mol^{-1} sec^{-1} in this case,[10] τ_0 at 6.1 *M* ketone is 4.7×10^{-10} sec. From our studies and data of Eaton[4] (Φ = 0.27 at 3.0 *M* ketone), k_d/k_r = 1.08 and $k_r = 3 \times 10^8$ l. mol^{-1} sec^{-1}.

(14) This second assumption is probably not strictly correct, although it is only necessary for our purposes that the rate constants for diffusion of the quencher away from the triplet do not differ greatly.

Table I. Results of Quenching of Ketone Triplets[a]

Ketone (E_T, kcal)	$k_q\tau_0$[b]	$k'_q\tau_0$[c]	k_q/k'_q
II, R = ethyl	0.29 ± 0.01[d]	0.019 ± 0.001	15.3
R = isobutyl	0.29 ± 0.01	0.021 ± 0.002	13.8
R = isoamyl	0.32 ± 0.02	0.031 ± 0.002	10.3
R = *n*-butyl	0.59 ± 0.04	0.048 ± 0.003	12.3
R = methyl	0.71 ± 0.02	0.075 ± 0.004	9.5
α-Santonin, I (68 ± 1)[e]	0.40 ± 0.06	0.096 ± 0.009	4.2
	(0.22 ± 0.02)[f]	(0.075 ± 0.005)[f,g]	(2.95)[f]
III (61–69)[h]	0.57 ± 0.04	0.24 ± 0.03[i]	2.4
II, R = H	2.31 ± 0.14	0.80 ± 0.02	2.9
IV (67 ± 1)[j]	10.7 ± 0.3	6.95 ± 0.33[k]	1.5
V (63 ± 1)[h]	34.1 ± 0.5	25.2 ± 1.2	1.35
VI (60 ± 1)[h]	107.1 ± 1.4	112.4 ± 6.0	1.0
Cyclopentenone (61 ± 1)[l]			
0.12 *M*	11.0 ± 0.6	14.0 ± 0.5	0.79
1.0 *M*	8.1 ± 0.3	9.6 ± 0.3	0.85
3.0 *M*	4.6 ± 0.1	4.5 ± 0.3 (5.0)[m]	1.02
6.1 *M*	2.1 ± 0.1	2.2 ± 0.1	0.96

[a] Determined by a competitive irradiation technique using a merry-go-round apparatus, high-pressure mercury lamp, Pyrex filters, benzene solutions, room temperature. Conversions in the blank were kept generally under 5% (and in no case beyond 15%) to prevent light absorption by products. In certain cyclohexadiene runs, the 366-nm line was isolated with a Corning 7-83 filter combination, and no difference was observed from runs with Pyrex filters. Analysis for product appearance by glpc with flame ionization detection using internal standards and calibration with known mixtures of reactant, products, and standard. [b] Quenching with 1,3-cyclohexadiene. [c] Quenching with *trans*-piperylene. [d] Standard deviation from least-squares straight line. Accuracy is estimated at better than 10%, from repeat determinations. [e] From emission spectra: ref 3 and M. H. Fisch and J. H. Richards, *J. Am. Chem. Soc.*, **85**, 3029 (1963). [f] Repeat determination at 366 nm using a different analytical technique. [g] *cis*-Piperylene, slope = 0.094 ± 0.004. [h] From studies with a graded series of sensitizers and quenchers. [i] Commercial mixture of *cis*- and *trans*-piperylenes. [j] From emission spectra: D. J. Patel and D. I. Schuster, *J. Am. Chem. Soc.*, **89**, 184 (1967), and H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967). [k] *cis*-Piperylene, slope = 6.0 ± 0.3. [l] By chemical spectroscopy and phosphorescence quenching.[11,12] [m] Reference 4.

to cyclohexadiene and k' to *trans*-piperylene, and k_{et} is the rate constant for the process $(D^* + A) \rightarrow D_0 + A^*$.[10]

From the relationship $k_q = \alpha k_{dif}$, where

$$\alpha = \frac{k_{et}}{k_{et} + 1/\tau_0 + k_{-dif}}$$

we have

$$\frac{k_q}{k'_q} = \frac{\alpha}{\alpha'} = \frac{k_{et}}{k'_{et}}\frac{(k'_{et} + 1/\tau_0 + k_{-dif})}{(k_{et} + 1/\tau_0 + k_{-dif})} = \frac{k_{et}}{k'_{et}}(1 - \alpha\beta) = \frac{1 - \alpha\beta}{1 - \beta}$$

where $k'_{et} = k_{et}(1 - \beta)$.

For long-lived triplets, $1/\tau_0$ is very small compared with k_{et} and k_{-dif}, so that α is independent of triplet lifetime, but for triplets of lifetime on the order of 10^{-10} sec, the terms are of comparable importance and α becomes a function of lifetime. The value of k_q/k'_q will increase as τ_0 and α decrease, approaching a limiting value of k_{et}/k'_{et}. According to this treatment, differential quenching should be observable if $\beta \neq 0$ with long-lived triplets whenever $\alpha \neq 1$, although as pointed out previously[10] these effects may be lost beneath the large experimental error often associated with such measurements, especially when α is close to unity.[15] Furthermore, this treatment requires that even for short-lived triplets $k_q = k'_q$ if $k_{et} = k'_{et}$, *i.e.*, if $\beta = 0$. The reason why $k_{et} \neq k'_{et}$ for the ketones in Table I is not established with certainty but may be associated with an orientational effect such as preferential energy transfer to a cisoid rather than a transoid or skew diene, perhaps due to orbital overlap. This should be clarified by work in progress with an extensive series of ketones and dienes in a variety of solvents, which may provide information on the preferred orientation of donor and acceptor in such a process. The generality of these observations remains to be seen.[16]

Acknowledgment. We are grateful to Professor Peter Wagner for providing details of his work prior to publication, and to him and Professor Graham Underwood of this department for stimulating and helpful discussions.

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(15) The assumption is made throughout that energy transfer is exothermic by at least 3 kcal/mol.

(16) A case of a steric effect in "exothermic" energy transfer has been noted by W. G. Herkstroeter, L. B. Jones, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4777 (1966).

(17) Fellow of the Alfred P. Sloan Foundation.

(18) American Cyanamid Summer Fellow, 1965; Frederick W. Miller, Jr., Fellow, 1967.

(19) National Science Foundation Predoctoral Trainee, 1967.

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A Novel Probe into the Simultaneity of Cycloaddition Reactions. The [2 + 2] and [2 + 4] Systems

Sir:

In spite of the tremendous amount of work that has been devoted to the mechanism of [2 + 4] cycloaddition reactions, the problem of the simultaneity of these processes still demands a great deal of attention from mechanistic organic chemists. While most of the experimental literature seems to favor a synchronous process,[1] and Woodward and Hoffmann predictions clearly concur with this point of view,[2] there are notable cases where evidence points to a nonsynchronous

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(1) J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967).

(2) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).