Tetrahedron Letters No.11, pp. 1301-1306, 1968. Pergamon Press. Printed in Great Britain.

THE NATURE OF QUENCHING OF KETONE EXCITED STATES USING HIGH CONCENTRATIONS OF DIENES.

THE REACTIVE ELECTRONIC EXCITED STATE OF α-SANTONIN(1)

David I. Schuster* and Arthur C. Fabian**

Department of Chemistry, New York University
University Heights, New York, N. Y. 10453

(Received in USA 3 November 1967)

It has recently been shown by Hammond and his co-workers(2) that it is possible to quench excited singlet states of aromatic hydrocarbons such as naphthalene and anthracene using a variety of cyclic and acyclic dienes. In many cases this quenching is surprisingly efficient (k_q as high as 2.5×10^9 l/mole-sec.), considering that this process is formally endothermic on the basis of spectroscopic singlet energies. These observations raise the important question of whether similar singlet quenching might also be an important process in the photochemistry of ketones. Thus, Zimmerman and Swenton(3) have questioned the rigorousness of the conclusion that triplet quenching is indeed involved, all or in part, particularly when very high concentrations of dienes are required in order for quenching to be observed, as in the photochemistry of 4,4-diphenylcyclohexadienone(3) and α-santonin.(4) We decided to obtain additional evidence to define the nature of the quenching process in the particular case of α-santonin, which has played such a key role in the development of modern organic photochemistry.(5)

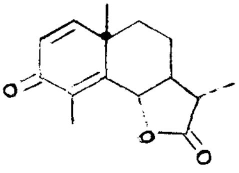
Previously, Fisch and Richards(4) had shown that the photoconversion of α-santonin (1) to lumisantonin (2) could be sensitized by benzophenone [E_T 68.5 kcal/mole], but not by Michler's ketone [E_T 61.0 kcal/mole],

---

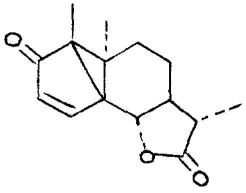
*Fellow of the Alfred P. Sloan Foundation

**American Cyanamid Summer Fellow, 1965; Frederick W. Miller, Jr., Fellow, 1967.

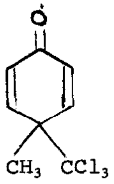
and that this conversion was "completely quenched" when piperylene was used as solvent. Curiously, these authors(4) also observed that



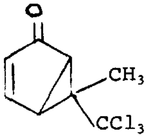
1



2



3



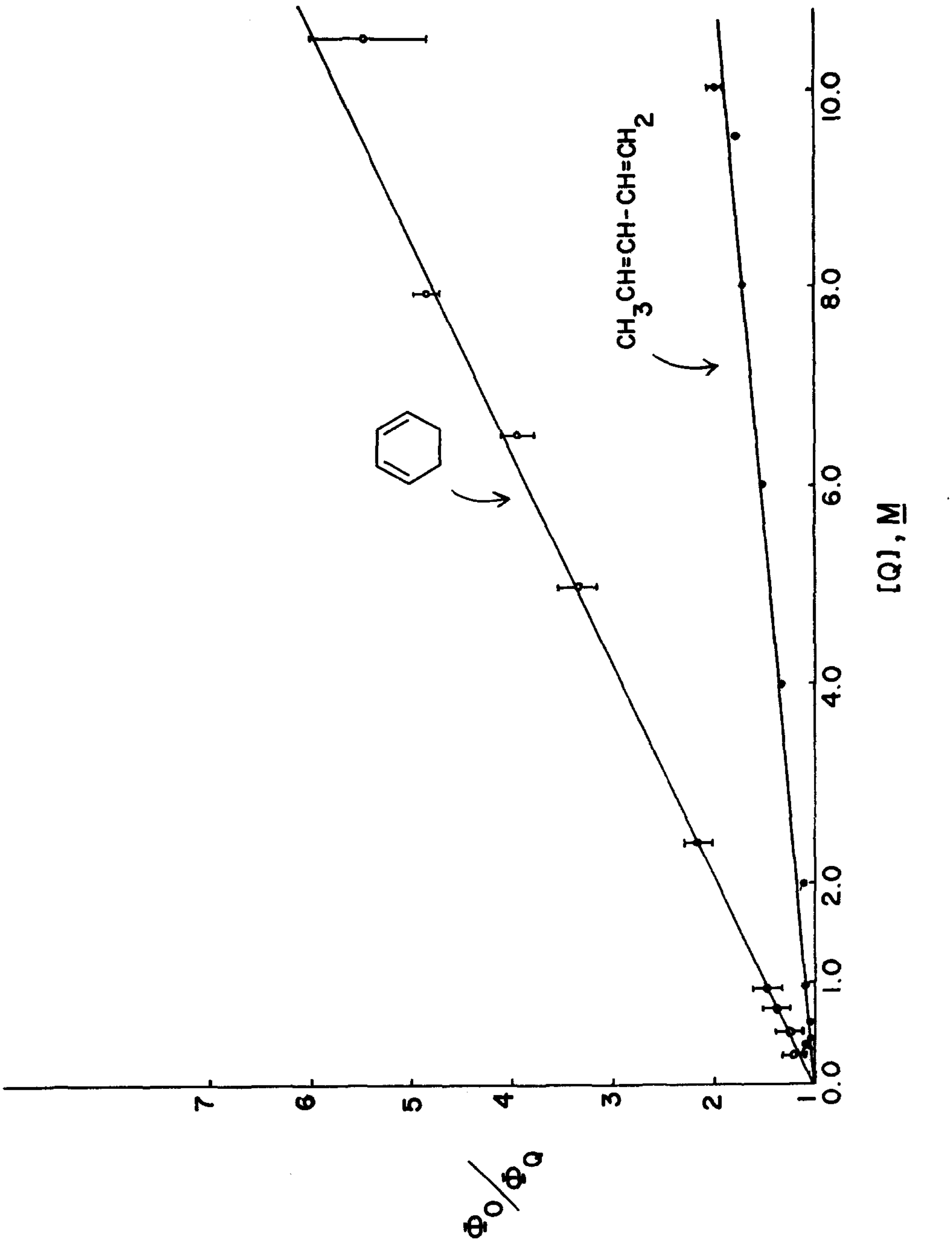
4

α-santonin did not cause the cis-trans isomerization of dilute solutions of piperylenes or stilbenes. On the other hand, Patel and Schuster(6) observed that the analogous conversion to lumiproduct 4 from the trichloromethyl dienone 3 could be quenched with dilute solutions (0.03 to 0.34 M) of piperylene, and a triplet lifetime of 1.5×10^{-9} sec. could be determined.

Irradiations of degassed (three freeze-thaw cycles) solutions of α-santonin in benzene containing varying amounts of piperylene or 1,3-cyclohexadiene were carried out on a merry-go-round(7) apparatus using a Hanovia 100-watt high pressure mercury arc and Pyrex filters. Conversions to lumisantonin were kept under 7%, as lumisantonin absorbs more strongly than α-santonin above 300 mu. Analyses for lumisantonin were made using gas-liquid partition chromatography (glpc) with internal standards.[#] The results, in terms of relative quantum yields for formation of lumisantonin, are shown in the Figure. The uncertainties represent average deviations of independent determinations. Both Stern-Volmer plots are linear over the entire range of concentrations up to solvent quencher, indicating (in the absence of unusual coincidence) that

---

[#] Analyses were on an F & M Model 810 Gas Chromatograph with flame ionization detection and disc integration. Lumisantonin analyses were on a 6-ft. 10% Apiezon L on Chromosorb W AW/DMCS column at 230° with benzil as internal standard. Cyclohexadiene dimer analyses were on a 5-ft. 10% XF-1150 on Chromosorb P column at 85° with acetophenone as internal standard.


Φ_0 / Φ_Q
1
2
3
4
5
6
7
0.0
1.0
2.0
4.0
6.0
8.0
10.0
[Q], M
$CH_3CH=CH-CH=CH_2$

quenching of only one excited state is being observed. This excited state was shown unequivocally to be the triplet state by a "triplet counting"(7) procedure using cyclohexadiene. Triplet sensitized photolysis of 1,3-cyclohexadiene is known to give a mixture of dimers(8) with quantum yield of 0.9 in the case of benzophenone sensitization.(8b) The dimers were isolated from large scale runs with santonin and were shown to be identical with those formed from benzophenone sensitization; spectral properties were in agreement with those previously reported.(8) When solvent cyclohexadiene was used to quench α-santonin, the amount of dimers produced (glpc analysis)# in duplicate runs was 95 and 98% of that expected if all the quenched lumisantonin arose from triplets which sensitized the dimerization of cyclohexadiene.## Thus, in the high concentration range, all quenching of santonin by cyclohexadiene is triplet quenching. From the linearity of the plot, this conclusion must be valid over the entire concentration range.

Using the usual Stern-Volmer expression(5c)

$$\frac{\Phi_0}{\Phi_Q} = 1 + \tau_s k_q[Q] = 1 + \frac{k_q[Q]}{k_r + k_d}$$

the rate constant for reaction (k_r) and the lifetime (τ_s) of the triplet can be calculated from the slope of the cyclohexadiene plot (0.48±0.02), assuming that the quenching is diffusion controlled.(5c,9) Using a value for k_q in benzene of 5×10^9 1/mole-sec.,(10) the triplet lifetime of santonin is found to be $1.0 \pm 0.2 \times 10^{-10}$ sec. Quantum yields for formation of lumisantonin in benzene and cyclohexadiene at 366 mu were determined to be 0.86±0.06 and 0.19±0.03, respectively. Assuming that all of the small observed inefficiency arises only in the triplet manifold by processes as yet undefined, the rate of rearrangement of santonin triplet, k_r, is found to be 8.6×10^9 sec.$^{-1}$

[##] Assuming Φ for this process is 0.9.(8b)

The slope of the Stern-Volmer plot for piperylene, 0.085±0.005, is different by a factor of six from that found using cyclohexadiene. From the work of Fisch and Richards,(4) a triplet energy for santonin of 68±1 kcal/mole is assigned. We have redetermined the phosphorescence emission spectra of α-santonin in ethanol and methylcyclohexane glasses at 77° K, in agreement with the earlier data.(4) Thus, energy transfer in solution from α-santonin to both cyclohexadiene [E_T 54.0 kcal/mole](5c,1) and piperylene [E_T 57-59 kcal/mole](5c,12) should be equally efficient, in contradiction with the experimental results. We tentatively ascribe this difference to an orientation factor which becomes observable on quenching of very short-lived triplets. Further speculation must await the results of further studies using a variety of quenchers and additional substrates.

In summary, these results <u>require</u> that the photorearrangement of α-santonin to lumisantonin proceeds entirely <u>via</u> the lowest triplet state of α-santonin. This triplet is extremely short-lived, and is <u>not</u> completely quenched even when the quencher is used as solvent. This result is in qualitative agreement with the observations made for 4,4-diphenylcyclohexadienone(3) and the trichloromethyl dienone <u>3</u>.(6) In the cases of <u>3</u> and α-santonin, and by implication the diphenyl dienone as well, singlet quenching is not observed, indicating that intersystem crossing from the singlet to the triplet manifolds is a very efficient process. The lack of quenching of singlets in these cases may be due to a combination of two factors: the singlets probably have even shorter lifetimes than those of aromatic hydrocarbons,(2) and the singlet quenching process is probably even more endothermic with these ketones than it is with aromatic hydrocarbons.(3) These results further demonstrate the utility of quenching techniques for assignment of configurations of excited states when used together with a quantitative analysis of the products derived from the quencher.

<u>Acknowledgment</u>. We are indebted to Dr. Angelo Lamola of Bell Telephone Laboratories for the emission spectra and for stimulating discussions. We are grateful for the support of this work by the U. S. Army Research Office (Durham) under Grant DA-ARO(D)-31-124-G812.

REFERENCES

1. Part XIV of a series on the photochemistry of unsaturated ketones in solution. Part XIII: D. I. Schuster, B. R. Sckolnick and F.-T. Lee, J. Am. Chem. Soc., in press.

2. L. M. Stephenson, D. G. Whitten, G. F. Vesley and G. S. Hammond, J. Am. Chem. Soc., 88, 3665 (1966); G. S. Hammond, Abstracts of the 20th National Organic Symposium of the American Chemical Society, Burlington, Vermont, June 1967.

3. H. E. Zimmerman and J. S. Swenton, J. Am. Chem. Soc., 89,906 (1967).

4. M. H. Fisch and J. H. Richards, Ibid., 85, 3029 (1963).

5. For reviews of the literature, see: (a) P. J. Kropp, Org. Photochem., 1, 1 (1967); (b) K. Schaffner, Adv. Photochem., 4, 81 (1966); (c) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, Inc., New York, N. Y., 1965. (d) O. L. Chapman, Adv. Photochem., 1, 323 (1963); (e) H. E. Zimmerman and D. I. Schuster, J. Am. Chem. Soc., 84, 4527 (1962).

6. D. J. Patel and D. I. Schuster, Ibid., 89, 184 (1967).

7. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).

8(a) D. Valentine, N. J. Turro, Jr. and G. S. Hammond, J. Am. Chem. Soc., 86, 5202 (1964); (b) D. H. Valentine, Ph.D. Dissertation, California Institute of Technology, Pasadena, Calif., 1966.

9. This assumption may not be entirely correct. See P. J. Wagner, J. Am. Chem. Soc., 89, 5715 (1967). Further work is in progress to test the assumption in this case.

10. P. J. Wagner and G. S. Hammond, Ibid., 88, 1245 (1966).

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

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