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THE MULTIPLICITY OF THE [1,3]-SIGMATROPIC PHOTOREARRANGEMENT OF VERBENONE TO CHRYSANTHENONE[1]

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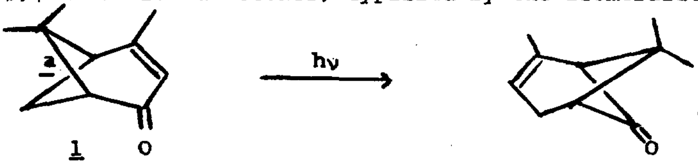
The photochemical allylic rearrangement of verbenone 1 to chrysanthenone 2, studied by Hurst and Whitham[4] and by Erman,[5] is the prototype of a general photochemical reaction involving [1,3]-sigmatropic shift of an alkyl moiety.[6] Only limited attention has been given to the multiplicity of the photorearrangement of α,β to β,γ-unsaturated ketones, typified by the isomerization of 1 → 2, and only in systems quite different structurally from 1.[7] The more closely related rearrangement of ketone 3 to 4 has been recently observed by Cargill, *et al.*[6], to proceed with complete loss of stereochemistry at the migrating carbon atom, suggesting a non-concerted rearrangement involving an intermediate diradical. Determination of the multiplicity of this rearrangement was not reported.[6] As noted[6], considerations of orbital symmetry lead to the prediction that concerted suprafacial allylic photorearrangements *via* the singlet excited state should occur with retention of stereochemistry at the migrating carbon atom. Current interest in the relationship of multiplicity and concertedness of photochemical rearrangements led us to further investigate the conversion 1 → 2, and we now report that this reaction originates exclusively from triplet excited states.



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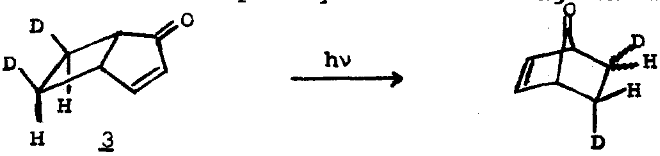

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Quenching of the photorearrangement of 1 to 2 in cyclohexane, benzene, and methanol by triplet energy transfer was studied using *trans*-piperylene (1,3-pentadiene) as quencher over the concentration range 0.012 to 1.31 M. Several runs were made in each solvent, and the linear form of the simple Stern-Volmer relationship (eq 1), relating the relative quantum yield for formation of

$$\Phi_0 / \Phi = 1 + k_q\tau_t \, [Q] \qquad (1)$$

chrysanthenone 2 to the quencher concentration [Q], was obeyed over the entire concentration range. The studies were made in Pyrex tubes using the merry-go-round technique with 3500 Å lamps in a Rayonet Chamber Reactor, with analysis by gas-liquid partition chromatography (glpc) on 10' x 1/8" columns of 20% DC-200 silicone oil on 70-80 mesh Anakrom ABS at 150°. The experimental results were subjected to a least squares computer analysis. The slopes and intercepts with deviations are given below:

Solvent	Number of Points	Slope, $k_q\tau_t$	Intercept
Cyclohexane	28	2.37 ± 0.19	1.10 ± 0.04
Benzene	7	1.69 ± 0.21	1.00 ± 0.06
Methanol	7	2.67 ± 0.48	1.10 ± 0.15

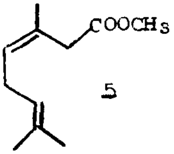
It was determined that the quenching of formation of 2 involved triplet energy transfer at least in part by studies using 1,3-cyclohexadiene (CHD) as quencher. The CHD dimers known to be formed only via transfer of triplet excitation to CHD[8] were formed in good yield on irradiation of degassed solutions of 1 in the presence of CHD. The ratio of dimers (glpc) was exactly the same as in benzophenone sensitized dimerization of CHD.

The lack of curvature in the Stern-Volmer plots indicates that the photorearrangement involves only triplet excited states as reactive intermediates, in the absence of fortuitous equation of various reaction parameters.[9] Assuming that quenching is occurring at close to the diffusion controlled rate, which seems likely from the results below, the triplet state lifetime is on the order of 10^{-9} seconds.

The above conclusions were confirmed by the results of experiments using a series of triplet sensitizers: β-acetonaphthone (E_T 59.3 kcal/mole), thioxanthone (E_T 65.5), benzophenone (E_T 68.5) and acetophenone (E_T 73.6).[10] The relative concentrations of verbenone 1 and sensitizers (1 fixed at 0.0067 M) were adjusted so that the sensitizer absorbed 95% of the incident light using the experimental arrangement described earlier. Irradiation of tubes containing sensitizers was carried out competitively with direct irradiation of solutions with the same concentration of 1, but without sensitizer. Adjusting for the difference in light capture (total optical density) of each tube, it was concluded that sensitization occurred if the conversion of 1 to 2 was greater than

5% of that in the unsensitized irradiation. It was found that β-acetonaphthone totally quenched the conversion of 1 → 2, and the amount of 2 formed in the thioxanthone tube was exactly accounted for on the basis of that portion of the light directly absorbed by 1. The amount of 2 formed in the benzophenone and acetophenone tubes indicated some triplet sensitization had definitely occurred, the efficiency greater with acetophenone than with benzophenone. Even with acetophenone, however, the amount of product 2 was considerably less than that expected if triplet energy transfer to 1 was 100% efficient. These results indicate that the triplet energy of 1 is probably upwards of 70 kcal/mole. Recently, it was determined that some substituted 2-cyclopentenones had triplet energies near 71 kcal/mole, and that in this case as well energy transfer from acetophenone was not entirely efficient.[11]

Photolysis of 1 in methanol under our conditions gave in addition to 2 the ester 5, which results from reaction of the ketene photoproduct 6 with methanol.[4,5] We studied the effect of piperylene in methanol on the efficiency of formation of 5 as well as 2, and found the quenching of the two products to occur to exactly the same extent: quenching of formation of 5 gave $k_q\tau_T = 2.84 \pm 0.50$, intercept 0.99 ± 0.15. Thus, we conclude that the [1,3]-sigmatropic shift to give 2 and the ring cleavage to give ketene 6 take place from the same triplet excited state, or thermally equilibrated triplet states. It has been shown by Erman[5] that 2 is formed from 1 in part *via* ketene 6.



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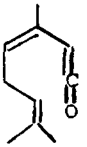

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In conclusion, the results of this study indicate that the photorearrangement of 1 to 2, either direct or *via* ketene 6, is a triplet state reaction. This is consistent with the conclusion reached by Cargill, *et al.*, on the rearrangement of 3 to 4 on the basis of stereochemical data. It appears, therefore, that in compounds such as 1 and 3 intersystem crossing to triplets is much more rapid than concerted [1,3]-sigmatropic shift from the singlet excited state, which should take place with retention of configuration, i.e., by a partial pivoting motion around bond a in verbenone 1. This conclusion is in contrast to the observation that [1,3]-sigmatropic shifts of acyl groups in photorearrangements of β,γ-unsaturated ketones are entirely singlet state reactions.[12]

ACKNOWLEDGMENT

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