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# EXCITED STATE PROPERTIES OF 3,4,5,6,7,8-HEXAHYDRONAPHTHALEN-2(1H)-ONE

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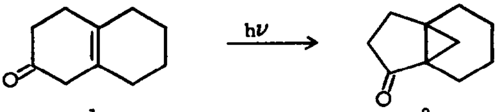
The photochemical transformation of the title compound (1) to cyclopropyl ketone 2 is a rare example of an oxadi-π-methane rearrangement occurring on direct irradiation.[2,3] We now report sensitization, quenching, and phosphorescence studies on 1 which reveal further complexities in its photochemistry.



1 2

The results of irradiating 1 with three photosensitizers are summarized in Table I. We have also found that triphenylene[4] (triplet energy $E_T = 67$ kcal mol$^{-1}$) and p-methoxyacetophenone ($E_T = 71$ kcal mol$^{-1}$) cause very slow disappearance of 1 and appearance of 2. If one postulates that $E_T$ of 1 is above 71 kcal mol$^{-1}$ but below that of acetone (80 kcal mol$^{-1}$), most of the sensitization results become understandable. However, the capacity of the n,π* triplet sensitizers, acetophenone and benzophenone, to destroy 1 deserves further attention.

Table I. Triplet Photosensitization of 1 in Benzene

| 1,Conc'n, M | Sensitizer | Conc'n, M | λ,nm | Φ(-1) | Φ(2) | % Reacted |
|---|---|---|---|---|---|---|
| 0.10 | Acetone | neat | 313 | 0.15 | 0.05 | 27 |
| 0.051 | Acetophenone | 0.20 | 366 | 0.057 | 0.00 | 28 |
| 0.050 | Benzophenone | 0.50 | 366 | 0.093 | 0.00 | 45 |

Attempts to isolate a product from these reactions always met with failure, for only a streak was observed on tlc and no volatile materials were detected by vpc. Suspecting that these reactive sensitizers were abstracting an allylic hydrogen from 1, we determined the rate constant (k) for quenching of acetophenone and benzophenone phosphorescence in acetonitrile by 1. The observed values were 3.4 x $10^8$ and 4.3 x $10^8$ M$^{-1}$ sec$^{-1}$, respectively, which are some three orders of magnitude faster than typical hydrogen abstraction rates.[5]

The interpretation of these results would be greatly facilitated if $E_T$ of 1 were known accurately. Hancock and Grider[6] have reported $E_T$'s in the range 60.9 - 73.7 kcal mol$^{-1}$ from phosphorescence spectra of a number of $\beta,\gamma$-unsaturated ketones ($\beta,\gamma$-UK's). Since phosphorescence is a process exhibited only by triplet states, a finite intersystem crossing yield is a prerequisite for observing it. However, independent evidence exists that many of the compounds studied by Hancock do not intersystem cross. Direct irradiation of norbornenone, for example, gives none of the triplet product[7], a result which we have confirmed. Similarly, 3-ethylidene-2,2,5,5-tetramethylcyclohexanone undergoes cis-trans isomerization only on triplet sensitization.[8] Since phosphorescence spectroscopy is an extremely sensitive technique, the possibility remains open that the intersystem crossing yield is a small, but finite, number. Ketone 1 intersystem crosses with high efficiency (see below); hence it should phosphoresce far more intensely than any previously studied compound. Instead, we observed only feeble emission from highly purified samples of 1 in several glassy solvents at 77K. Although the onset of phosphorescence was in the region of 80 kcal mol$^{-1}$, we are unconvinced that it was actually due to 1.

The possibility that a quenching impurity is responsible for our failure to observe emission from triplet 1 can be quickly rejected. Not only does theory show that phosphorescence quenching in a rigid medium requires large quencher concentrations[9], but we find that addition of 0.1 M piperylene to 0.1 M p-methoxyacetophenone in ethanol at -196° reduces the phosphorescence intensity by only 30%. On the other hand, phosphorescence spectroscopy is extremely sensitive to *emitting* impurities and it seems likely that such impurities were responsible for most of the $\beta,\gamma$-UK spectra reported earlier.[6]

We can, however, estimate that the triplet energy of $\beta,\gamma$-unsaturated ketones is between 74 and 78 kcal mol$^{-1}$ without resorting to phosphorescence experiments. The lowest singlet state, which is $n,\pi^*$, lies at about 86.7 kcal mol$^{-1}$, judging from the usual 330 nm onset of absorption in simple $\beta,\gamma$-UK's. The $n,\pi^*$ singlet-triplet splitting[10] should be somewhere between that of acrolein (1614 cm$^{-1}$) and formaldehyde (2996 cm$^{-1}$), placing the $n,\pi^*$ triplet within 2 kcal of acetone triplet (80 kcal mol$^{-1}$). However, the *lowest* triplet state is probably $\pi,\pi^*$ in character[11], so that it could easily lie below 78 kcal mol$^{-1}$. The high efficiency of acetone as a photosensitizer is consistent with this estimate. The fact that energy transfer from acetophenone to 1 is an order of magnitude slower than diffusion controlled places a 74 kcal mol$^{-1}$ lower limit on $E_T$ of 1.

If $E_T$ of 1 lies above that of acetophenone, we can readily understand the inability of this sensitizer and benzophenone to transform it to 2. But why is 1 such a rapid triplet quencher and why is it destroyed by aromatic ketones? We suggest that interaction of 1 and many other $\beta,\gamma$-UK's with aromatic ketone triplets can give an excited complex which may decay or lead to reaction of sensitizer with $\beta,\gamma$-UK. In the present case, benzophenone and acetophenone follow the latter pathway, whereas decay seems to predominate in two other $\beta,\gamma$-UK's.[12]

Further studies on 1 were designed to measure its intersystem crossing efficiency ($\Phi_{isc}$) by the sensitized dimerization of cyclohexadiene (D).[13] A straightforward kinetic analysis shows that a plot of the reciprocal of the dimerization quantum yield $(\Phi_{di})^{-1}$ versus the reciprocal of the diene concentration ($[D]^{-1}$) should be linear with the intercept equal to $(\Phi_{isc})^{-1}$. However, Figure 1 shows that this simple scheme is not followed in the case of compound 1. The sharp decrease in $\Phi_{di}$ at high diene concentration suggests that D interacts with singlet ketone, probably by formation of a singlet excited complex.[14] This phenomenon can be described by equation (1),

$$\frac{1}{\Phi_{di}} = \left[\frac{1}{\Phi^{o}_{isc}} + \frac{k^{S}_{q}}{k_{isc}}[D]\right]\left[1 + \frac{1}{k^{T}_{q}\tau_{T}}\,\frac{1}{[D]}\right]\left[1 + \frac{0.029}{[D]}\right] \qquad (1)$$

where $k^S_q$ is rate at which D quenches ketone singlets, $k^T_q$ is the analogous parameter for ketone triplets, and $\tau_T$ is the lifetime of these triplets. The last term, which allows for the effect of diene concentration on the inherent efficiency of dimerization, was cancelled in our work by running a benzophenone sensitized dimerization for each concentration of cyclohexadiene.

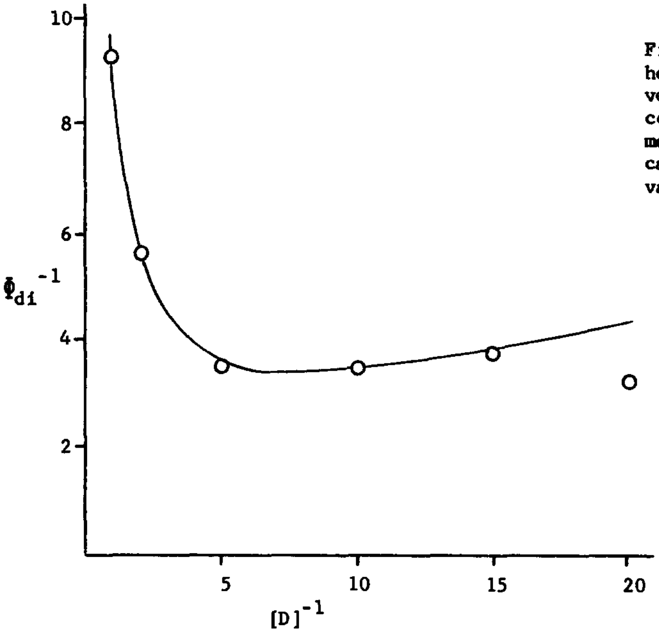


Fig. 1 Reciprocal of the cyclohexadiene dimerization quantum yield versus the reciprocal of cyclohexadiene concentration.[15] Circles are experimental points and the solid curve is calculated from equation 1 using the values given in the text.

A good fit to the experimental points occurs with $\Phi^o_{isc} = 1.0$, $k^s_q/k_{isc} = 7.3$ and $k^T_q\tau_T = 10$ (cf. Figure 1) but $\Phi^o_{isc}$ could be as low as 0.5 and $k^T_q\tau_T$ as high as 29. The value of $k^s_q/k_{isc}$ is firm but independent values for these rate constants cannot be extracted from the data. However, making the reasonable assumption that triplet transfer from 1 to D is diffusion controlled, we obtain the first estimate of the triplet lifetime of a β,γ-unsaturated ketone, ~4 nsec.

It is noteworthy that both sensitization and quenching of ketone 1 are complicated by excited complex formation.

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15. The point at lowest diene concentration is subject to the greatest experimental uncertainty. In another run, it was found considerably higher than shown here.