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OBSERVATION OF A KETYL RADICAL ON FLASH EXCITATION OF A 2,5-CYCLOHEXADIENONE

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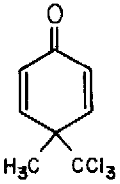
Although the photochemistry of 2,5-cyclohexadienones has been a continual focus of intensive study during the last fifteen years,[1-4] flash photolysis has played no role to date in the characterization of reaction intermediates in these systems. Triplet states of these ketones are very short-lived (on the order of 10^{-8} to 10^{-10} sec)[3b,4] due to very rapid unimolecular modes of reaction, and have not been detectable directly using either microsecond or nanosecond techniques.[4d] Although zwitterions have been implicated in dienone photochemistry[1] and have been trapped nucleophilically,[5] they too have not been observed directly at ambient temperatures by flash methods. We now report that on flash excitation of dienone 1 in hydrogen donating solvents, a transient is observed whose absorption spectrum and decay characteristics strongly suggest that it is the ketyl radical 2.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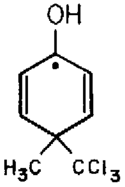
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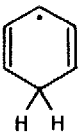
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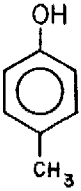
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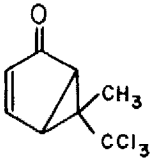
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Flash excitation (360 J flash, $\tau \sim 40$ µsec) of 0.1 M solutions of 1 in 2-propanol, ethyl ether or cyclohexane, degassed by five freeze-pump-thaw cycles on a high vacuum line, generated long-lived transient absorption between 500-600 nm which decayed by clean first order kinetics. The lifetimes of the transient in these solvents, as obtained from the slopes of plots of log OD vs. time, are 2.1×10^{-4}, 2.1×10^{-4} and 2.4×10^{-4} sec^{-1}, respectively. The absorption spectrum of the transient in 2-propanol, obtained point by point from values of the optical density 0.4 msec after the flash, is given in Figure 1. This spectrum is quite similar to the spectrum recently reported[6] for cyclohexadienyl radical 3 which showed maxima at 512 and 554 nm. We assign our transient absorption to ketyl radical 2; the spectral shifts compared to 3 are readily accounted for in terms of substitution of a hydroxy group on the central carbon and the change from a nonpolar to polar solvent. The assignment is supported by the following considerations.

We have shown that p-cresol 4 is a triplet-derived product of steady state irradiation of 1 in hydrogen donating solvents,[3a,b] and presumably arises by the following sequence:

$$\underline{1} \xrightarrow{h\nu} {}^{1}\underline{1}^{*} \rightarrow {}^{3}\underline{1}^{*} \xrightarrow{SH} S\cdot + \underline{2} \tag{1}$$

$$\underline{2} \rightarrow \text{p-cresol} + \cdot CCl_3 \tag{2}$$

Products derived from $\cdot CCl_3$ as well as solvent-derived radicals S· are observed. We detect no transient absorption using nanosecond techniques on flash excitation of 1 in benzene, carbon tetrachloride or *tert*-butyl alcohol, solvents in which 4 is not formed. The transient lifetime is independent of solvent polarity, suggesting it is a radical and not an ionic species. Finally, the addition of oxygen (4×10^{-4} *M*)or di-*tert*-butyl nitroxide (DTBN) (2×10^{-4} *M*) to dienone solutions in cyclohexane completely wipes out transient absorption. However, on repeated flashing of such solutions, the transient absorption reappears and eventually recovers its full intensity (Figure 2). The transient decay lifetime as well as its intensity increases on repeated flashing; the data analysis indicates that both O_2 and DTBN reduce the transient intensity more than its lifetime, indicating that a precursor to the transient is intercepted as well as the transient itself in reactions which consume O_2 and DTBN irreversibly. Interestingly, 1,3-cyclohexadiene (CHD) reduces the intensity but not the lifetime of the transient, indicating CHD intercepts a precursor to the transient but not the transient itself. The most likely precursor is the dienone triplet excited state. Indeed, the slope of the straight line plot of relative transient absorption intensity vs. CHD concentration agrees well with slopes of quenching by CHD of product formation from 1 in steady state photolyses, attributed previously to triplet quenching.[4d]

These results are complementary to our previous report that triplet quenching and radical scavenging are both involved in the photochemistry of 1 in H-donor solvents,[7] and define more precisely the roles of CHD, O_2 and DTBN. For example, CHD has been shown to trap radicals on irradiation of 1 in 2-propanol,[7] and during the thermal generation of p-cresol 4 from benzoyl peroxide and dienone 1 in 2-propanol.[8] The present results require that CHD intercepts chain carriers other than ketyl radical 2, such as $\cdot CCl_3$ and $(CH_3)_2COH$.

Finally, activation parameters for decay of 2 in 2-propanol have been determined from experiments at different temperatures using jacketed cells connected to a constant temperature bath.

Table 1. Activation Parameters for Transient Decay[a]

Run	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu	E_{act} kcal/mole	Log A
1	7.4 ± 0.3	-17.4 ± 1.0	8.0 ± 0.3	9.5 ± 0.3
2	7.4 ± 0.3	-17.6 ± 1.1	8.0 ± 0.3	9.4 ± 0.5

[a] All data are reported using a 95% confidence limit on the error bar.

The parameters from two totally independent runs are given in Table 1. The low unimolecular rate is found to be due to a highly unfavorable entropy of activation and not a high activation enthalpy. The latter was expected to be small since two stable species, an aromatic ring system and a stabilized radical, are the reaction products. We can only speculate as to the reason for the large negative $\Delta S^{\ddagger}$. An intriguing possibility is that radical 2 does not directly fragment into p-cresol and "free" trichloromethyl, but that an intermediate pi-complex is formed; the principle of microscopic reversibility would then require that such a species be invoked in the addition of trichloromethyl (and perhaps other radicals) to p-cresol (and perhaps other aromatic molecules).

Attempts are being made to detect and characterize 2 by ESR spectroscopy.

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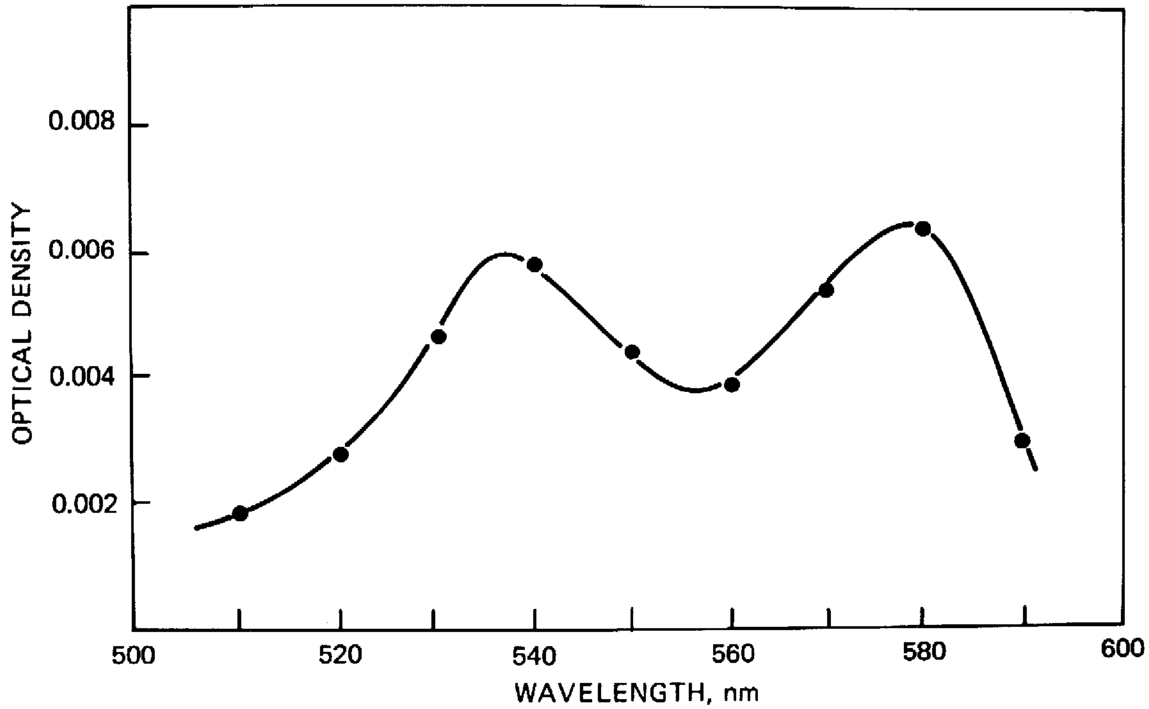

Figure 1. Absorption spectrum of transient formed by flash excitation of 0.10 M solution of dienone 1 in 2-propanol.

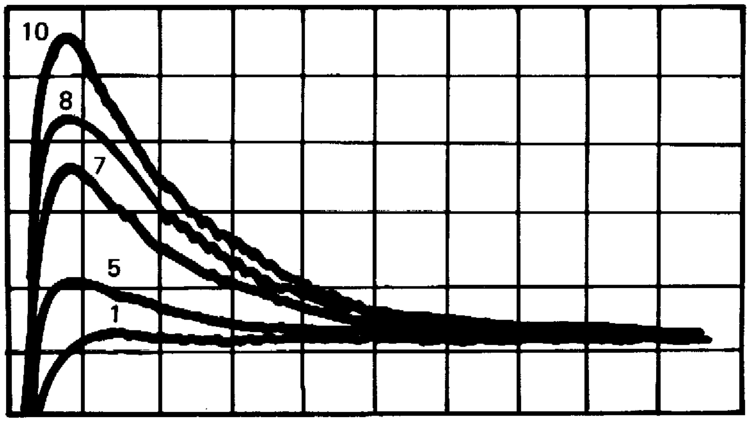

Figure 2. Decay of transient absorption at 580 nm from flash excitation of 0.1 M dienone 1 in cyclohexane after addition of 2 ul of DTBN to solution (total volume 70 ml). Decay shown as a function of number of flashes following addition of DTBN. Conditions: flash capacitance 20 µf, charge 6 kV, sensitivity 0.5 V/cm (full deflection 20 V), time scale 50 µs/cm.