Optical Rotation Measurements. The optical rotatory dispersion of 3-methyl-5-bromo-1-cyanoadamantane was measured in the 365–600-nm range on a Rudolph manual spectropolarimeter Model 200S/340/80AQ6 modified as described elsewhere.[28] The 1-dm polarimeter tube containing the solution was thermostated by means of water circulating around the polarimeter trough. The temperature was measured with an iron–constantan thermocouple inserted in a glass well in the filling port. Rotation readings were repeated five to ten times, giving standard deviations of the mean in the range 0.6–1.3 mdeg, or 1–3% of the mean rotation as limited by the available quantity of the compound. Other optical rotation measurements were made in part on a Bendix Model 143A electronic polarimeter, and in part by Dr. Donald Fraembs of the Bendix Corporation on Bendix Models 1184-00, S/N L40511017 and 1164-00, S/N L40411018.

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Intermediate Species in the Flash Excitation of a Conjugated Ketone

Göran Rämme, Robert L. Strong, and Herbert H. Richtol

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181.

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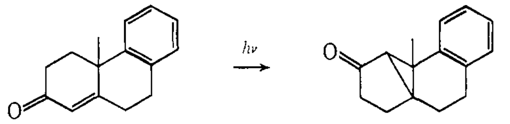
Abstract: Excited states and intermediates of the conjugated cyclohexenone 7-keto-13-methyl-5,6,7,9,10,13-hexahydrophenanthrone have been studied flash spectrophotometrically. Two transient species differing in spectral and decay characteristics are observed, the longer lived being the ketyl radical formed by hydrogen-atom abstraction. The shorter lived intermediate is presumed to be a triplet state, but is not the triplet precursor to the isomeric rearrangement or reduction reactions; this latter species was not observed directly, but was detected by triplet–triplet energy transfer to naphthalene. Neither directly observed species was optically active within the limit of detection of the flash spectropolarimeter, although optical activity is retained in the isomeric photoproduct.

Conjugated cyclohexenones undergo rearrangements photochemically,[1] although at a much lower quantum efficiency than for corresponding cyclohexadienones.[2] A particularly interesting example is 7-keto-13-methyl-5,6,7,9,10,13-hexahydrophenanthrone I which rearranges to the bridged isomeric photoketone II.

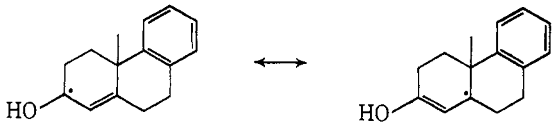


(1)

I II

Photoexcitation of either of the enantiomeric forms of I leads to at least 95% retention (but opposite rotation) of the optical activity in II[3] showing that the rearrangement is stereospecific; it cannot take place through complete fission of the 1,10 bond leading to an intermediate having a plane of symmetry, but most involve 4–10 and 1–5 concerted bond formation also.[2] This rearrangement to II proceeds through a triplet state,[2] which must also be optically active and therefore possibly amenable to studies by the flash spectropolarimetric technique.[4] Since I is an α,β-unsaturated ketone, it is an inherently dissymmetric chromophore and therefore should have a much greater rotational strength than corresponding inherently symmetric carbonyl chromophore-containing molecules.[5] (This high rotational strength depends on the angle of skewness of the carbonyl-containing ring, however, which may be significantly altered in the excited state.)

Ketones also undergo photoreduction by way of triplet-state hydrogen abstraction from the solvent molecules, the extent of abstraction being influenced by the nature of the substrate as well as by the rate of isomeric rearrangement. Zimmerman, *et al.*,[2] found that in *t*-butyl alcohol the isomerization (1) was the only irreversible reaction, whereas in isopropyl alcohol a pinacol was formed by dimerization of the radical



(2)

formed by hydrogen abstraction.

The present work was undertaken to determine the nature of the intermediate(s) in the rearrangement and abstraction reactions by direct flash spectrophotometry.

Experimental Section

The flask spectrophotometric apparatus, modified for transient polarimetric measurements, has been described.[4,6] Except for a few runs in which the effect of flash light intensity was determined by varying the flash discharge energy, all of the data reported here

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[1] K. Schaffner, *Advan. Photochem.*, 4, 81 (1966).

[2] H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. S. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 159, 1965 (1966).

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[4] P. A. Carapellucci, H. H. Richtol, and R. L. Strong, *ibid.*, **89**, 1742 (1967).

[5] A. Moscowitz, *Proc. Roy. Soc.*, **A297**, 16 (1967).

[6] R. L. Strong and H. H. Richtol in "Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Almqvist and Wiksell, Stockholm, 1967, p 71.

were obtained with 900-J flashes (12.5 μF, ±6 kV) with peak intensity at *ca.* 7 μsec and a half-width of 11 μsec.

The reaction cells were cylindrical (25-mm i.d., 100-mm analyzing light path), constructed of either Pyrex or fused quartz with optically flat fused windows. The cell was enclosed in a black Bakelite compartment with quartz or Pyrex rectangular (1 × 3.5 × 15 cm inside dimensions) filter cells interposed between the cell and the two flash tubes. Two filter solutions were used: filter solution A (saturated solution of $CoCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ in acetone), with a uv cutoff at 320 $m\mu$ and maximum transmittancy at 350 $m\mu$ (50% in 1 cm); and filter solution B (saturated solution of $CoSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ in water), which transmits from 230 to 360 $m\mu$ with maximum transmittancy at 300 $m\mu$ (85% in 1 cm).

The racemic phenanthrone I (Aldrich) and zone-refined naphthalene (Fisher Reagent) were used without further purification. Samples of the enantiomers of I were very kindly supplied by Professor O. L. Chapman. All solvents were Fisher Certified grade. *t*-Butyl alcohol was refluxed and distilled twice over sodium through a 48-cm Vigreux column, the second being at a high reflux ratio. Carbon tetrachloride and benzene were purified by procedures previously described.[7] Isopropyl alcohol and *n*-hexane (Spectrograde) were used without further purification. All solutions to be flashed were outgassed by at least six freezing, pumping, and thawing cycles in a grease-free Pyrex bulb attachment to the reaction cell which was removed from the vacuum system by sealing off prior to use.

Results

Spectra and Decay Kinetics of Transient Species. The ultraviolet absorption spectrum of the phenanthrone I consists of two main bands: the intense π–π^* transition at 237 $m\mu$ (log ϵ 3.14), and the weaker n–π^* absorption at *ca.* 330 $m\mu$ (log ϵ 1.69) in nonpolar solvents but demonstrating the usual blue shift in polar media.[8] In addition, there is an unresolved shoulder at 273 $m\mu$. Accordingly, where possible (depending on the ultraviolet cutoff of the particular solvent used) solutions were flashed with both filter systems (A and B), in the former case absorption by the solution being limited to n–π^* excitation.

Flash excitation of I in all of the solvents used (benzene, *t*-butyl alcohol, isopropyl alcohol, *n*-hexane, or carbon tetrachloride) led to at least two detected transitory species of quite different decay times and absorption spectra. The relative amount of long-lived species (half-life *ca.* 0.1 sec in *t*-butyl alcohol) increased with increasing hydrogen donor ability of the solvent, but in all cases it was a very minor component of the transient signal in the visible region; the absorption spectrum of this long-lived intermediate, measured both at 0.4 and 20 msec after flash initiation, was structureless and increased with decreasing wavelength to 340 $m\mu$ (the lowest wavelength at which measurements with this system could be made) without passing through a maximum. These observations are consistent with the assignment of this absorption to the protonated ketyl radical formed by hydrogen abstraction (eq 2), which is the precursor for pinacol formation.[2]

The spectrum of the short-lived species in benzene, obtained at 75 μsec after flash initiation and corrected for the slight amount of absorption due to the long-lived species as determined at 400 μsec, consisted of a broad, structureless band with maximum at *ca.* 430 $m\mu$. (Implied in this correction is the assumption that both long- and short-lived species are produced independently and that all of the long-lived component is produced before 75 μsec, *i.e.*, essentially during the flash.) The decay of absorbance so corrected was first order in each solvent over at least a sixfold change in concentration, but was slightly dependent on the viscous nature of the solvent and concentration of the phenanthrone solute, as shown in Table I. This relative minor dependence on concentration of I may be due to a quenching impurity in the original reactant material, or to self-quenching through hydrogen abstraction from I ($k \sim 5 \times 10^5$ l. mole^{-1} sec^{-1}).

Table I. First-Order Rate Constants for Short-Lived Component at 25°

Concn, *M*	Solvent	Viscosity, cP	$k \times 10^{-3}$ sec^1
0.7×10^{-3}	*n*-Hexane	0.3	7.0
7.2			12.7
0.8	Benzene	0.6	4.4
7.4			8.7
3.0	Carbon tetrachloride	0.9	7.8
7.1			9.7
0.8	Isopropyl alcohol	2.1	2.9
3.0			4.9
7.2			6.0
7.3			6.4
0.8	*t*-Butyl alcohol	3.4	2.6
3.0			4.4
7.3			5.3
7.5			5.4

Effects of Oxygen on the Short-Lived Species. Molecular oxygen is known to be a very efficient quencher of excited triplet states of organic molecules, the effect being in fact appreciably greater than predicted for a diffusion-controlled reaction and suggesting static quenching over relatively large distances.[9]

Various pressures of oxygen were introduced into a previously outgassed solution of I in *t*-butyl alcohol from a metered side-arm volume, and the effect on the apparent first-order decay of the short-lived species was determined. Assuming the usual Stern–Volmer treatment for relatively low concentrations of the added quencher

$$k_{obsd} = k_1 + k_q[O_2] \qquad (3)$$

where k_1 is the first-order decay rate in the absence of oxygen, k_q is the observed bimolecular quenching rate constant, and $[O_2]$ is the oxygen concentration in solution. The solubility of oxygen in *t*-butyl alcohol was not measured; assuming, however, that the Ostwald absorption coefficient for oxygen is the same in *t*-butyl alcohol as in *n*-butyl alcohol (0.2100 at 6.4 Torr and 25°[10]), $k_q = 1 \times 10^9$ l. mole^{-1} sec^{-1}, in reasonable agreement with the diffusion-controlled constant predicted by the Debye relation assuming a continuous medium of viscosity η.

$$k_q = \frac{8RT}{3000\eta} = 2 \times 10^9 \text{ l. mole}^{-1} \text{ sec}^{-1} \qquad (4)$$

Effect of Other Quenchers on the Short-Lived Species. Naphthalene (E_T = 60.9 kcal[11]) quenches both the isomeric rearrangement reaction 1 and the hydrogen-abstraction process with approximately equal efficiency,[2]

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suggesting that both processes probably occur *via* the excited triplet state. To ascertain the effects of energy transfer to naphthalene on the production and lifetime of the short-lived species, flash spectrophotometric experiments were carried out at different concentrations by adding various aliquots of outgassed naphthalene from break-seal side arms to an outgassed *t*-butyl alcohol solution of I in the photoexcitation cell; direct excitation of naphthalene was completely prevented by using filter solution A (uv cutoff at 320 mμ) in the flash excitation light system. Triplet sensitization of the naphthalene occurred, as evidenced by the appearance of the known triplet–triplet absorption maxima at 390 and 410 mμ. As shown in Table II, however, the effect of this energy transfer on the decay of the observed short-lived species (measured at 500 mμ, where there is no naphthalene transient triplet–triplet absorption) is negligible. Furthermore, the lifetime of the naphthalene triplet is decreased with increasing concentration of I (the quenching rate constant $k_q = 7 \times 10^5$ l. mole^{-1} sec^{-1} being well below that for diffusion control), while the amount of the short-lived excited state of I is increased by the presence of naphthalene, approximately by a factor of 1.7 over the naphthalene concentration range given in Table II.

Table II. Decay of Observed Short-Lived Species in *t*-Butyl Alcohol as a Function of Naphthalene Concentration[a]

Naphthalene concn, $M \times 10^3$	$k \times 10^{-3}$ sec^{-1}
	7.0
2.3	5.8
9.8	5.1
44.0	4.8
66.0	5.2

[a] Concentration of I = 7.4×10^{-3} *M*.

Carbon tetrachloride is a very efficient quencher of luminescence,[12] and direct π,π^* singlet excitation of naphthalene in CCl_4 yields no triplet–triplet absorption. The naphthalene triplet state can be sensitized in CCl_4 by I, however, with a lifetime only slightly less than that measured in hydrocarbon solvents of comparable viscosity in keeping with the concurrent quenching by I. Similar results were obtained with the naphthalene–benzophenone–CCl_4 system; thus the benzophenone triplet (λ_{max} 520 mμ,[13,14] confirmed in this work) can be produced in CCl_4 by direct excitation in the n,π^* singlet absorption band and intersystem crossing, but it is quenched by naphthalene with diffusion-controlled efficiency and the naphthalene triplet produced with unquenched kinetic decay. It would therefore appear that carbon tetrachloride may only selectively quench the π,π^* singlet state as in naphthalene (probably by direct chemical reaction) and thus serve as a possible reagent for excited singlet-state identification.

Attempts to quench the observed short-lived species with other lower energy quenching molecules have been inconclusive. Thus, pyrene (E_T = 48.7 kcal[11]) at a concentration of 6.9×10^{-3} *M* appears to decrease the concentration of the excited state of I by approximately a factor of 2 (measured 60 μsec after flash initiation), but the large overlap of the pyrene triplet–triplet and the phenanthrone 430-mμ bands, the relatively long lifetime of the pyrene triplet in *t*-butyl alcohol ($\tau \sim 260$ μsec), and the presence of pyrene excited state dimers and complexes at this concentration[15] make this observation doubtful and preclude any valid interpretation of the kinetic data.

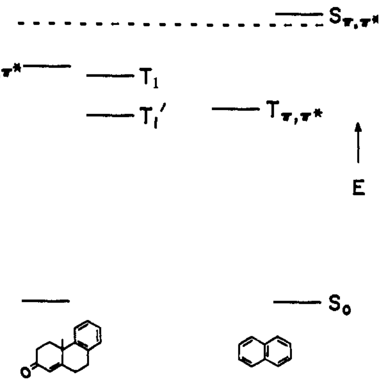

Figure 1. Relative energy levels for the phenanthrone I and naphthalene systems. The dotted line is the lower wavelength cutoff of filter solution A.

Discussion

The simultaneous sensitization of the long-lived species plus sensitization and quenching of the naphthalene triplet clearly indicate that at least two triplet states are produced by photoexcitation of I, only one being directly observable by flash spectrophotometry. (The same conclusion has recently been arrived at by Chapman and coworkers with similar cyclohexenones, using, however, quite a different experimental technique, and by others for comparable aromatic systems.[16–18]) A possible energy scheme, consistent with the results reported above, is given in Figure 1.

The undetected triplet sensitizes the π,π^* triplet of naphthalene, and therefore is assigned to T_1. Since naphthalene quenches the isomeric rearrangement and H-atom abstraction reactions, T_1 is also assumed to be the precursor intermediate triplet state for these products. Although the exact electronic nature of this state is not known, if it is an n,π^* triplet state then the very low quantum yield from this reactive state for hydrogen abstraction even in solvents with easily abstractable hydrogen atoms (for example, 0.002 in isopropyl alcohol[2]) must result from either a very short lifetime for T_1 (estimated by Zimmerman to be *ca.* 0.3 μsec[2]) or from a very inefficient n,π^* intersystem crossing relative to alternate intersystem crossing and/or internal conversion processes.

The fact that naphthalene, while quenching T_1, actually increases somewhat the concentration of T_1' (the observed 430-mμ species) without affecting the decay characteristics of T_1' indicates that T_1 and T_1' are formed by independent paths and that the decay of T_1 is not directly to T_1' but must be to S_0. This would seem to preclude T_1 being the π,π^* triplet of the con-

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[17] R. N. Griffin, *Photochem. Photobiol.*, 7, 159 (1968).

[18] B. Stevens and M. F. Thomaz, *Chem. Phys. Letters*, 1, 535 (1968).

jugated carbonyl moiety (which would then require the $T_1 \rightarrow T_1'$ process to be very rapid, of the order of 10^{-12} sec), although the intersystem crossing from the n,π^* singlet state to the π,π^* triplet should be much more efficient than the corresponding crossing to the n,π^* triplet.[19]

One possible interpretation of the nature of the T_1' state is that it is a π,π^* triplet state of the aromatic moiety of I, produced by the intramolecular energy transfer from the conjugated carbonyl chromophore such as occurs with 4-(1-naphthylalkyl)benzophenone[20] or 4-hexenone-2.[21] In this case, however, in the absence of appreciable conjugation between rings in the molecule it might be expected that the triplet energy of the aromatic ring would be close to that of *o*-xylene, or approximately 20 kcal higher than that for T_1' from the positive but relatively inefficient quenching of the naphthalene triplet. Another possibility of T_1' is that it is the triplet state of an intramolecular charge-transfer interaction[22] from the aromatic ring to the carbonyl group, although lack of spectral solvent effects and reactivity and the relatively weak electron-donating capacity of an aromatic group make this a less plausible description.

Regardless of the nature of T_1', the lack of quenching by naphthalene clearly indicates that it is not the precursor to the observed products of the photorearrangement and reduction reactions. Extensive attempts to detect transient anomalous optical rotation in the region of the 430-mμ band were unsuccessful within the limits of accuracy and detection of the flash spectropolarimeter, only a slight (<0.01°) negative rotation being observed and attributable to the disappearance of the normal ground-state dispersion on excitation of the + enantiomer. This also suggests that the observed triplet–triplet absorption is more appropriately associated with the aromatic ring rather than with the more highly rotating skewed carbonyl-containing ring,[5] although as pointed out above this may also result from a large reduction of the skewness of the ring on excitation without actual over-all irreversible loss of optical activity.

Luminescence. Zimmerman[2] reports a luminescence spectrum of the phenanthrone I with a 0′–0 band at 401 mμ, which he assigns to the phosphorescence emission from T_1. Two weak emission bands with maxima at 390 and 510 mμ were observed in this work using either the commercially available racemic phenanthrone or the resolved enantiomers, but neither band was affected by atmospheric oxygen or the physical state of the solvent (room temperature benzene fluid or 77°K 1:4 isopentane–methylcyclohexane glass). Furthermore, the two emission bands were strongly dependent on the exciting radiation wavelength, maximum emission resulting from illumination at 320 and 400 mμ, respectively; this latter is energetically well below the ground-state singlet–singlet absorption band of I and suggests some persistent fluorescing impurity or photodecomposition product in the phenanthrone material. Lack of appreciable phosphorescence emission resulting from direct singlet excitation at 320 mμ further indicates that intersystem crossing to T_1 is very inefficient relative to crossing to T_1'.

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