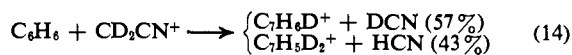


is exothermic by 71 or 64 kcal/mol.¹⁶ The $C_7H_7^+$ species is also formed in the acetonitrile-benzene system (eq 13-15) by the electrophilic attack of CH_2CN^+



on benzene; again, this represents the product of a loss of a small neutral from the intermediate addition product. Scrambling data indicate that more hydrogen is lost from the activated complex than from the acetonitrile-derived species than would be expected on the basis of complete randomization of all eight hydrogens.

Ion cyclotron resonance is of great value in demonstrating that some ion-molecule products in these mixtures are indeed products of initial electrophilic aromatic addition, apparently similar to the first step in solution electrophilic aromatic substitution, after which gaseous and solution pathways diverge. Further studies of electrophilic aromatic substitution reactions, substituent effects on them, and the structure of $C_7H_7^+$ formed by ion-molecule reactions will be discussed in full papers.

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N. Y., 1963, p 453; (b) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, **90**, 2983 (1968).

(15) F. H. Field, *ibid.*, **89**, 5328 (1967).

(16) Data taken from (a) "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969; (b) Handbook of Chemistry and Physics, 49th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968.

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Flash Photolysis of a Conjugated Cyclohexenone. A Reinvestigation¹

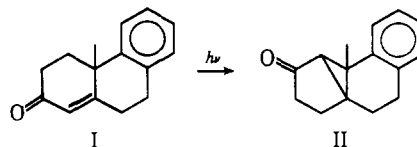
Sir:

The results of a flash photolytic investigation of the conjugated cyclohexenone I were recently reported by Rämme, Strong, and Richtol (RSR).² These results were most unusual and surprising, especially in relation to the steady-state photolytic studies previously reported on I by Zimmerman and Chapman and their

(1) Part XXVIII of a series on the photochemistry of unsaturated ketones in solution. Part XXVII: D. I. Schuster and W. C. Barringer, *J. Amer. Chem. Soc.*, in press.

(2) G. Rämme, R. L. Strong, and H. H. Richtol, *ibid.*, **91**, 5711 (1969).

coworkers^{3,4} and studies of other cyclohexenones reported by Bellus, Kearns, and Schaffner⁵ and by Schuster and Brizzolara.⁶



It had been found earlier that the inefficient photoisomerization $I \rightarrow II$ as well as photopinacolization of I in 2-propanol proceed from a triplet state (or two triplet states in thermal equilibrium) which can be quenched by naphthalene.³ The lifetime of the triplet in benzene from the quenching data was estimated as $\sim 10^{-8}$ sec.³ Phosphorescence at low temperature showed a 0-0 band at 401 nm (71 kcal/mol).³ This value is in agreement with the phosphorescence observed more recently with a number of other fused-ring cyclohexenones,⁷ which has been convincingly attributed⁷ to emission from the lowest π, π triplet, which in these systems is below the lowest n, π triplet state.

On the basis of the above, it was surprising that on flashing I in a variety of solvents, including good as well as poor hydrogen donors, two transients were observed.² A short-lived transient was observed (τ 100-400 μ sec), λ_{max} 430 nm, which exhibited first-order decay, and which could be quenched by oxygen but *not* by naphthalene. In fact, the lifetime of the naphthalene triplet was decreased as the concentration of I was increased, indicating triplet energy transfer from, rather than to, naphthalene. The second transient, which showed a long lifetime on the order of many milliseconds, was a minor component in the visible region, and increased in intensity at lower wavelengths. Finally, the emission data previously reported³ could not be duplicated, and the weak emission observed by RSR² was tentatively ascribed to an impurity. In order to explain these observations, RSR² postulated that the reactions of I proceeded exclusively *via* an upper triplet state, and that there was a lower triplet (the short-lived transient) which was unreactive, energetically situated below the lowest naphthalene triplet. The long-lived transient was assumed to be the protonated ketyl radical formed by hydrogen abstraction, although the formation of this species (albeit in decreased amounts) in poor hydrogen donor solvents passed without comment.

Since all other cyclohexenones studied thus far³⁻⁶ have very close-lying n, π and π, π triplets, with the lowest triplet located approximately 70 kcal/mol above the ground state,^{3,5} it seemed most strange that I should have such different characteristics. It seemed to us that the most reasonable explanation for the observations of RSR² was that the observed transients

(3) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *ibid.*, **88**, 159, 1965 (1966).

(4) O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *ibid.*, **88**, 161 (1966).

(5) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

(6) D. I. Schuster and D. F. Brizzolara, *J. Amer. Chem. Soc.*, **92**, 4357 (1970).

(7) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968); G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).

were due to some contaminant in their sample of I. Indeed, the racemic phenanthrone in their study was utilized as obtained from the supplier (Aldrich) without further purification. We found that the melting point of I was raised from 84.5–85.5° to 90–90.5° on recrystallization of the same commercial material. Accompanying the change in melting point was a substantial decrease in the ultraviolet absorption of I in the long-wavelength band at 345 nm, where the flash excitation of I had been performed.² While no impurity was detectable in I by nmr, analysis by gas chromatography indicated some minor contaminants not found in the purified sample.

The flash photolytic behavior of I in the microsecond and millisecond time range was studied using standard techniques.⁸ The behavior reported by RSR² could be quantitatively reproduced using the commercial, impure sample of I. However, no transients could be observed in flashing purified samples of I in benzene, 2-propanol, and carbon tetrachloride, monitoring from 40 μ sec after the flash at wavelengths from 350 to 430 nm, working at very high sensitivity.⁹ Furthermore, with the impure samples in 2-propanol a gradual decrease in the amount of the short-lived transient was observed, suggesting gradual consumption of the impurity by hydrogen abstraction reactions. Surprisingly, there was only a slight decrease in the amount of the long-lived transient under these conditions.

There is no doubt that the transients observed by RSR² are due in fact to some contaminating impurity, which can be removed by recrystallization. The exact nature of the impurity is purely conjecture at this time, but from its triplet energy (<61 kcal/mol) and rate of disappearance in hydrogen-donating solvents, a reasonable candidate is a substituted 1,2- or 1,4-naphthoquinone.^{10,11}

The most important conclusion is that the observations of RSR² have absolutely no bearing on the photochemistry of I in particular and cyclohexenones in general.

Acknowledgment. We gratefully acknowledge partial support of this study by the Petroleum Research Fund, administered by the American Chemical Society.

(8) Experiments were made on an FP-2R apparatus supplied by Northern Precision Co., Ltd., London, using a krypton-filled flash lamp without filters. The data were obtained with 360-J flashes. Solutions were exhaustively degassed at high vacuum by the freeze-thaw technique.

(9) The sensitivity was much higher than that needed to detect transients with impure I.

(10) Triplet-state energies of 1,2- and 1,4-quinones are usually 50–57 kcal/mol above the ground state. See A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N. Y., 1969, pp 93 and 239.

(11) Transient absorption has been found on flash photolysis of some 1,2- and 1,4-quinones in the 400–500-nm region, attributed to the triplet state and/or the semiquinone radical. For leading references, see: D. R. Kemp and G. Porter, *Chem. Commun.*, 1029 (1969); P. A. Carapellucci, H. P. Wolf, and K. Weiss, *J. Amer. Chem. Soc.*, **91**, 4635 (1969); E. J. Land, *Trans. Faraday Soc.*, **65**, 2815 (1969).

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A Photochemical Exchange Reaction of Michler's Ketone

Sir:

Michler's ketone, 4,4'-bis(*N,N*-dimethylamino)benzophenone, is reported to be photochemically reactive in cyclohexane solvent ($\phi_{\text{disappearance}} = 0.3$) but unreactive in isopropyl alcohol.^{1,2} The solvent effect was attributed to a change in configuration of the reactive triplet state from n, π^* to π, π^* . Reactivity in cyclohexane was characterized as hydrogen atom abstraction by the nonbonding orbital of the carbonyl; however, characterization of the products has not been achieved. Other investigators agree that Michler's ketone is photoreactive in cyclohexane but conclude that the photoprocess does not involve hydrogen atom abstraction leading to pinacol.^{3,4}

We have observed a photochemical exchange reaction of Michler's ketone which we feel describes the primary photochemical process. When Michler's ketone (0.010 *M*) is irradiated in benzene solution in the presence of ethanethiol (0.32 *M*), the quantum yield of disappearance of Michler's ketone is retarded by a factor of 3. Irradiation of Michler's ketone (0.01 *M*) in the presence of ethanethiol-*S-d* (0.32 *M*) exchanges up to 12 hydrogens of Michler's ketone for deuterium, ϕ_{exchange} equal to 0.09. The nmr spectrum of recovered Michler's ketone indicates that the methyl hydrogens are exchanged. In the absence of light no exchange is observed. The quantum yield for hydrogen-deuterium exchange is dependent on Michler's ketone concentration.⁵ A plot of reciprocal of quantum yield *vs.* reciprocal of Michler's ketone concentration is linear, with least-squares slope and intercept of 0.047 ± 0.003 *M* and 5.3 ± 1.3 , respectively. The reaction is efficiently quenched by 1,3-cyclohexadiene, giving a linear Stern-Volmer plot, least-squares slope 275 ± 46 l./mol.

The two quantum yield plots indicate that the primary photochemical process initiating the observed hydrogen-deuterium exchange is a reaction of excited-triplet-state Michler's ketone with ground-state Michler's ketone. Since the intercept of the plot of reciprocal of quantum yield *vs.* reciprocal of Michler's ketone concentration is greater than unity beyond experimental error, an energy wasting step must be included in a description of the mechanism. Bimolecular energy wasting (self-quenching) has been reported for several aromatic ketones with lowest energy π, π^* triplet states.⁸ A general mechanism consistent with the data is presented in Scheme I,

(1) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965); **62**, 3375 (1966).

(2) P. Suppan, *Ber. Bunsenges. Phys. Chem.*, **72**, 321 (1968).

(3) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965).

(4) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966).

(5) Quantum yield measurements were conducted at 28° with a rotating photochemical apparatus⁶ at 366 nm using potassium ferrioxalate actinometry.⁷ The per cent deuterium incorporation was measured by mass spectrometry at 13 eV.

(6) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(7) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(8) O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969).