versible addition of radicals[17] discouraged further work along this line. The photodimerization of 1,3-cyclohexadiene, which is known to occur only by triplet sensitization,[5,18] proved to be a somewhat more fruitful approach. The quantum efficiency of photodimerization (Φ_{di}) should increase with diene concentration because energy transfer is better able to compete with decay of the short-lived ketone triplet; on the other hand, the efficiency should decrease as the added diene interferes more with intersystem crossing. In fact, Φ_{di} increased with diene concentration, reaching a limiting value of 0.15 at 0.5 *M* quencher. This behavior is consistent with an intersystem crossing yield near unity, in agreement with the results for acetone.[10]

To confirm that decarbonylation occurred from the triplet state, sensitization experiments were performed. The fact that xanthone (E_T = 74.2 kcal) gave no detectable CO formation was entirely unexpected, since its triplet energy is 2.0 kcal above that reported[2] for **1**. Even more surprising was the result that **1** did not quench the type II process in butyrophenone[19] (E_T = 74.7 kcal) nor the photoreduction of acetophenone[20] (E_T = 73.6 kcal) by isopropyl alcohol. On the other hand, acetone (E_T = 80 kcal)[10] irradiated at 313 nm did appear to sensitize decarbonylation of **1** under conditions where the sensitizer was absorbing 93% of the light. Considered along with the absorption and emission spectra, these results cast considerable doubt on the published triplet energy of **1**. The overlap of the uv absorption and the fluorescence spectrum seen in Figure 2 occurs at about 325 nm, while the phosphorescence 0-0 band is at 398 nm, in agreement with the literature value.[2] This leads to a value of nearly 5700 cm^{-1} for the singlet–triplet splitting, which is unreasonably large for a ketone.[21]

Further investigation revealed that the observed phosphorescence of **1** was due to an impurity. Carefully purified **1** showed no emission, but after exposure to air and light, it gave the phosphorescence spectrum in Figure 2, *which is identical with that obtained from benzaldehyde.* Moreover, injection of old samples of **1** into the LKB gas chromatograph–mass spectrometer gave a peak with the same retention time and mass spectrum as benzaldehyde. A value of 79 kcal for E_T of **1** is more realistic, since it would be consistent with the sensitization experiments, it would lead to a more reasonable singlet–triplet splitting, and it would explain the observation of Robbins and Eastman[4] that decarbonylation of **1** is partially quenched in benzonitrile (E_T = 77 kcal) as solvent.

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[18] D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **90**, 5145 (1968).

[19] P. J. Wagner and A. Kemppainen, *ibid.*, **90**, 5896 (1968); J. Pitts, Jr., D. Burley, J. Mani, and A. Broadbent, *ibid.*, **90**, 5900 (1968).

[20] S. Cohen, P. Laufer, and W. Sherman, *ibid.*, **86**, 3060 (1964).

[21] S. P. McGlynn, F. J. Smith, and G. Cilento, *Photochem. Photobiol.*, **3**, 269 (1964).

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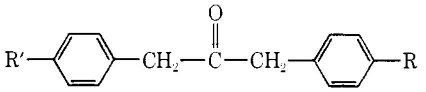
Received May 19, 1970

Photodecarbonylation in Solution. I. Quantum Yields and Quenching Results with Dibenzyl Ketones

Sir:

Although the solution-phase photodecarbonylation of a number of cyclic ketones[1] has been examined, the possibility of alternative intramolecular processes in cyclic systems has complicated a mechanistic understanding of the process. Only a few noncyclic ketones, which might be expected to lack these problems, have been observed to decarbonylate in solution.[2] In fact, the quantum yield has been reported for only one such photodecarbonylation.[2a] Although 1,3-diphenyl-2-propanone (dibenzyl ketone) (**1a**) has been observed to lose carbon monoxide nearly quantitatively when irradiated, the mechanism and efficiency of this reaction have not been clearly elucidated. We wish to report the results of our investigation of the nature of the excited state and efficiency of the photodecarbonylation for dibenzyl ketone (1,3-diphenyl-2-propanone, **1a**) and some of its derivatives (**1b**–**1e**).



1a, R = R′ = H
b, R = R′ = CH_3
c, R = H; R = OCH_3
d, R = R′ = OCH_3
e, R = R′ = CN

Quinkert[2b] reported detecting no photoproducts other than bibenzyl (1,2-diphenylethane) when dibenzyl ketone was irradiated in benzene until gas evolution ceased. At lower conversions, we were unable to detect any other photoproduct by chromatographic methods. However, contrary to expectations, irradiation of the ketone (**1a**) in benzene with 313-nm light[3] did not cause any reduction in the absorption at that wavelength during the first 20% of reaction (based on ketone consumption).[5] Consequently, the quantum yield[8] (Table I), determined at 20% conversion, is somewhat low.

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[1] (a) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966); (b) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Amer. Chem. Soc.*, **84**, 1220 (1962); (c) D. I. Schuster, R. R. Scholnick, and F. T. H. Lee, *ibid.*, **90**, 1300 (1968).

[2] (a) N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968); (b) G. Quinkert, K. Opitz, W. W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963).

[3] For this study, degassed 0.05 *M* solutions of the ketones were sealed in Pyrex and irradiated with the 313-nm light isolated from a medium-pressure Hg lamp with a chromate–carbonate[4] filter.

[4] P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

[5] The formation of only a 1 × 10^{-5} *M* solution of the "photoby-product" with a molar extinction coefficient of 2 × 10^{5} would cause the absorbance of the sample solution at 313 nm to remain constant. This represents only a 0.02% yield (based on initial ketone). It may be noted that photoby-products with such extinction coefficients have been encountered in the photolysis of benzophenone[6] and azocumene.[7] An extensive spectroscopic and chromatographic investigation of the photolysis of dibenzyl ketone produced no conclusive evidence about the nature of the photoby-product. However, in none of these experiments was any material other than bibenzyl produced in excess of 0.1%.

[6] N. Filipescu and F. L. Minn, *J. Amer. Chem. Soc.*, **90**, 1544 (1968).

[7] S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

[8] Duplicate product quantum yields were determined on the basis of glpc signal areas relative to hexadecane as an internal standard. Duplicate benzophenone–benzhydrol actinometers were irradiated simultaneously with the sample solutions in a Hammond merry-go-round.[9]

Table I. The Quantum Yields for the Photodecarbonylation of Some Dibenzyl Ketones in Benzene

	Compound	$\Phi_{\text{diphenylethane}}$
1a	1,3-Diphenyl-2-propanone	0.70 ± 0.10
1b	1,3-Bis(4-methylphenyl)-2-propanone	0.71 ± 0.11
1c	1-(4-Methoxyphenyl)-3-phenyl-2-propanone	0.66 ± 0.10[a]
1d	1,3-Bis(4-methoxyphenyl)-2-propanone	0.65 ± 0.14
1e	1,3-Bis(4-cyanophenyl)-2-propanone[b]	<0.02[c]
1a	1,3-Diphenyl-2-propanone[b]	0.71 ± 0.11

[a] Sum of the three possible phenylethanes which were obtained in the (statistical) 1:2:1 ratio. [b] In acetonitrile. [c] Limit of detection by nmr.

From the data in Table I, it appears that neither *p*-methyl nor *p*-methoxy substitution has an appreciable effect on the quantum yield for photodecarbonylation. Di-*p*-cyano substitution, on the other hand, completely suppresses photodecarbonylation. Acetonitrile, which was required to solubilize this ketone (**1e**), was found to have no effect on the photoreaction of the unsubstituted ketone (**1a**) (Table I). In fact, prolonged irradiation of ketone (**1e**) in acetonitrile provided no significant change in the nmr spectrum[11] of the solution.

It would appear that the n-π^* band of ketone (**1e**) is being photoexcited by the 313-nm irradiation on the basis of a shoulder band at 295 nm in its ultraviolet spectrum. The spectra of benzonitrile and the unsubstituted ketone (**1a**), which are in agreement with those in the literature,[12] indicate that the singlet energy of the latter is considerably larger. However, the triplet energies reported for benzonitrile[13] (E_T = 77 kcal/mol) and the ketone (**1a**)[14] (E_T = 72.2 kcal/mol), which are based on phosphorescence spectra under different conditions, were sufficiently close to suggest the possibility of internal triplet quenching in the dicyano ketone. To test this hypothesis, the unsubstituted ketone (**1a**) was photolyzed in benzonitrile with the result of pronounced quenching (Table II).

Table II. Relative Quenching Efficiencies of the Photodecarbonylation of Dibenzyl Ketone

Quenching system	(**1a**), initial, $M \times 10^2$	% reaction quenched[a]
Benzene	4.96	0
0.88 *M* biphenyl (in benzene)	5.42	12
Benzonitrile (12.5 *M*)	5.48	41[b]

[a] Based on ketone consumed in benzene. [b] Corrected for absorption by quencher.

The fact that the photodecarbonylation is not completely quenched at this concentration implies inefficient quenching. This requires either an endothermic process or a triplet with an extremely short lifetime. (The possibility of singlet-state decarbonylation is ruled out on the basis of the failure of the dicyano ketone (**1e**) to lose carbon monoxide.) Since biphenyl (E_T = 69.5 kcal/mol)[15] was also found inefficient in quenching the photodecarbonylation (Table II), the latter explanation is favored.[16]

If one assumes that only one excited state is being quenched, the Stern–Volmer equation may be used to approximate the order of magnitude of the lifetime of that state. With biphenyl as quencher, a value of 10^{-11} sec is obtained in this manner. A similar lifetime is obtained for benzonitrile as quencher if k_{diff} is assumed to be $\sim 10^9$ l. mol^{-1} sec^{-1} and the possibility of "nearest neighbor" quenching is neglected.

The failure of the dicyano ketone (**1e**) to decarbonylate reflects the high intramolecular "concentration" of the cyanophenyl groups in the molecule. Since benzonitrile itself is relatively unreactive when photoexcited,[18] the lack of alternative photoproducts is not surprising.

In summary, we have found that the photodecarbonylation of dibenzyl ketones occurs very efficiently from an extremely short-lived quenchable triplet.

Acknowledgments. The authors would like to thank Drs. J. I. Brauman, L. J. Altman, and L. M. Stephenson for their many helpful comments during the course of this work. We are indebted to the National Science Foundation Traineeship Program for financial support.

The quantum yield for this actinometer was calculated to be 0.84 on the basis of the work of Moore and Ketchum.[10]

(9) R. S. N. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

(10) W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).

(11) Owing to the unusual polarity characteristics of this compound, no satisfactory glpc conditions for analysis of this photolysis were found.

(12) (a) M. Ramart-Lucas, *Bull. Soc. Chim. Fr.*, **5**, 710 (1936); (b) M. Ramart-Lucas and M. F. Salmon-Legagneur, *ibid.*, **51**, 1076 (1932).

(13) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

(14) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(15) P. J. Wagner, *ibid.*, **89**, 2820 (1967).

(16) Since this work was completed, Dr. P. S. Engel (private communication) has found that the phosphorescence attributed to dibenzyl ketone is actually due to traces of benzaldehyde. On the basis of sensitization and quenching experiments, he has shown that dibenzyl ketone photodecarbonylates primarily from a triplet with E_T = 70 kcal/mol.[17] We are indebted to Dr. Engel for discussion of his work prior to publication.

(17) P. S. Engel, *J. Amer. Chem. Soc.*, **92**, 6074 (1970).

(18) R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966, p 198.

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Received May 19, 1970

Photodecarbonylation in Solution. II. Trapping of Intermediates in the Photolysis of Dibenzyl Ketone

Sir:

We have previously shown[1] that dibenzyl ketones photodecarbonylate in solution with high quantum efficiency *via* an extremely short-lived triplet state. In this communication, we will present evidence for a stepwise mechanism for this process.

In the photolysis of 1,1,3-triphenyl-2-propanone (**1**) in benzene, Quinkert[2] observed a statistical (1:2:1) distribution of product ethanes **2**, **3**, and **4** isolated in a 93% yield. This result clearly supported a free-radical mechanism but did not permit differentiation between concerted and stepwise processes for photo-

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(1) R. H. Eastman and W. K. Robbins, *J. Amer. Chem. Soc.*, **92**, 6076 (1970); the same photolysis conditions were used in this paper.

(2) (a) G. Quinkert, K. Opitz, W. W. Weirsdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963); (b) G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1964).