(broad unresolved multiplet, *ca.* 1 H), and 0.56 ppm (*ca.* 3 H, unresolved multiplet) consistent with the presence of a cyclopropane moiety bearing four hydrogens and two additional protons absorbing at unusually high field. Gorgosterol[2] and 9,11-seco-gorgost-5-ene-3,11-diol-9-one[15] also exhibit high-field ($\delta \sim 0.27$ ppm) noncyclopropyl proton absorption; other instances of high-field absorption by methylene protons proximate to cyclopropane and epoxide rings have also been reported.[16] Irradiation[17a] at δ 0.56 ppm (100 MHz) changes the apparent distorted triplet at δ 0.20 ppm to what appears to be a broadened doublet, $J \simeq 7$ Hz.[17b] Further decoupling experiments ($CDCl_3$) revealed that the broad signal at δ 3.35 ppm (1 H), ascribable to a proton attached to a carbon bearing oxygen, was coupled to the lowest field portion of the allylic proton absorption in agreement with the 3β-hydroxyl-Δ^5 partial structure suggested by rotational data (see above). Also consistent with the 3β-hydroxy-Δ^5 structure and a normal steroid nucleus is the presence of only one vinyl hydrogen absorption (δ 5.33 ppm, 220 MHz, $CDCl_3$) and two quaternary methyl signals, δ 0.66 and 1.09 ppm. Doublet methyl signals were observed at δ 0.91 ($J \simeq$ 6.5 Hz), 0.94 ($J \simeq 6.5$ Hz), 0.99 ($J \simeq 6.0$ Hz), and 1.01 ppm ($J \simeq 6.0$ Hz) and, since mass spectral evidence cited above supports a C-19 nucleus, these four secondary methyl groups must be part of the side chain. The structure **3** which we propose for the C-29 sterol is compatible with all of the above data. The nearly identical chemical shifts observed for the cyclopropyl methylene protons strongly suggest *trans* substitution for that ring since this configuration would provide essentially equivalent chemical shielding of these protons.[18] Further efforts are under way to clarify this point as well as to determine the absolute configuration of **3**.

Although it is possible that 23-demethylgorgosterol is a biosynthetic dead end, this sterol may be an intermediate in the biosynthesis of gorgosterol from a Δ^{22} precursor. The latter possibility provides further stimulation of our ongoing search for other new sterols related to gorgosterol and 23-demethylgorgosterol.

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[14] Multiplicity description is rendered difficult by virtue of the fact that these protons conform to an AA'XX' combination which can display a complex pattern; *cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon, New York, N. Y., 1965, p 392 ff.

[15] Private communication from Dr. A. J. Weinheimer of data presented at IUPAC Meeting, Riga, Latvia, June 1970.

[16] *Cf.*, for example, R. S. Boikess and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 343 (1963); P. R. Jefferies, R. S. Rosich, and D. E. White, *Tetrahedron Lett.*, 1853 (1963).

[17] (a) We are grateful to the Joelco Co., Medford, Mass., for carrying out the decoupling experiments; acquisition of decoupling data was rendered difficult by the limited amount of sample available for spectral analysis. (b) The converse double-irradiation experiments are as yet inconclusive due to the partial overlap of the lower field cyclopropyl absorption with the C-18 methyl and one of the unidentified upfield hydrogen resonances.

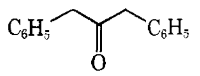
[18] D. E. Minnikin, *Chem. Ind.* (*London*), 2167 (1966).

[19] Recipient of a National Institutes of Health Special Fellowship (GM 13941) while on sabbatical leave at Woods Hole Oceanographic Institution (1969–1970) from the University of Oklahoma; to whom correspondence should be addressed.

Photochemistry of Dibenzyl Ketone

Sir:

Because the reported[1] photolability of dibenzyl ketone (**1**) seemed inconsistent with its inclusion in a table[2] of potential triplet photosensitizers, we were prompted to investigate the photochemistry of this compound. The following unusual results have emerged: (1) photodecarbonylation in solution is very efficient and proceeds from the triplet state, (2) the lifetime of this triplet state is shorter than that of the singlet, and (3) the triplet energy of **1** is considerably higher than the reported value of 72.2 kcal.



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By comparison of the rate of gas evolution from **1** with that from 2,3-diazabicyclo[2.2.1]heptene-2, whose nitrogen quantum yield is known[3] to be unity, it was determined that Φ_{CO} is 0.7 at 313 nm in benzene at 30°. This number must be taken as a minimum however, since a uv spectrum of the irradiated solution showed enhanced absorption in the 300-nm region. The cause of this absorption is not presently known; however, since we have confirmed that CO is produced in 100 ± 1% yield,[1] it must be due either to a compound which loses CO or to one produced in very small amounts.

In order to determine the nature of the excited state undergoing decarbonylation, quenching studies with two dienes were carried out. The results shown in Figure 1 indicate that 1,3-cyclohexadiene decreases the efficiency of CO formation more than it inhibits ketone disappearance. This effect, which was also noted in more concentrated solutions of 1,3-pentadiene, is attributed to capture of short-lived phenylacetyl radicals by diene. Robbins and Eastman[4] have reported capturing phenylacetyl radicals using a stable nitroxide free radical as scavenger.

The fact that dienes inhibit the disappearance of starting material is strong evidence for quenching of an electronically excited state. Although this state would traditionally be taken as a triplet, recent studies[5-8]

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[1] G. Quinkert, K. Opitz, W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963).

[2] W. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 86, 4537 (1964).

[3] B. Solomon, T. Thomas, and C. Steel, *ibid.*, **90**, 2249 (1968).

[4] W. K. Robbins and R. H. Eastman, *ibid.*, **92**, 6077 (1970).

[5] L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, 16, 125 (1968).

[6] T. R. Evans and P. A. Leermakers, *J. Amer. Chem. Soc.*, **91**, 5898 (1969).

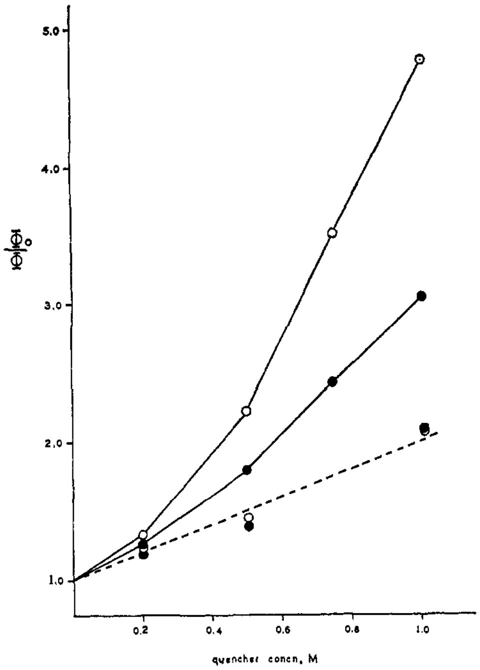

Figure 1. Stern–Volmer plot for quenching of dibenzyl ketone decarbonylation, [1] = 0.10 *M*: ○, carbon monoxide formation; ●, ketone disappearance; —, 1,3-cyclohexadiene; -----, 1,3-pentadiene.

indicate that dienes can interfere with intersystem crossing. A diagnostic test for such interactions is the effect of added quencher on the fluorescence of the sensitizer.

As shown in Figure 2, dibenzyl ketone exhibits easily detectable (Φ_f = 0.04)[9] fluorescence whose lifetime in benzene is τ_S = 3.6 nsec.[11] Addition of dienes causes a substantial decrease in the fluorescence intensity, as seen in Table I. No ground-state interactions between ketone and dienes were detected in the uv spectra nor was the shape of the ketone fluorescence spectrum altered by addition of diene. The value of k_q calculated for di-*tert*-butylnitroxide agrees excellently with other diffusion-controlled measured maximum values in benzene.[12]

Table I. Quenching of Dibenzyl Ketone Fluorescence in Benzene[a]

Quencher	$k_q\tau_s$[b]	k_q[e]
1,3-Pentadiene mixed isomers	0.21	5.9×10^7
1,3-Cyclohexadiene	1.7[c]	4.7×10^8
Di-*tert*-butylnitroxide	21.2[d]	5.9×10^9

[a] Solutions not degassed, excitation at 320 nm, emission at 400 nm, [1] = 0.01 *M*. [b] Stern–Volmer slope for fluorescence quenching. [c] The same value was obtained from the decrease in singlet lifetime. [d] Corrected for trivial absorbance by quencher. [e] Calculated from experimental lifetime.

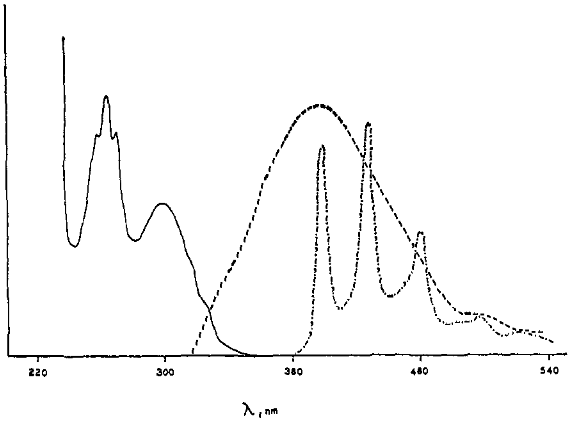

Figure 2. Absorption and emission spectra of dibenzyl ketone: (—) uv absorption in isooctane, λ_{max} 294 nm, ε 234; (-----) fluorescence in isooctane at 25°; (-·-·-·) phosphorescence in MCIP glass at 77°K.

Since 1,3-pentadiene inhibits dibenzyl ketone disappearance much more than it quenches its fluorescence, decarbonylation occurs to a considerable extent and perhaps exclusively from the triplet state. In contrast, other photodecarbonylations in solution appear to proceed *via* the singlet state.[13] After correction for singlet quenching by 1,3-pentadiene, one can calculate that the triplet quenching constant $k_q\tau_T$ is on the order of 0.7. If k_q is taken as 5×10^9 M^{-1} sec^{-1},[12,14] τ_T would be 10^{-10} sec, a value so short as to preclude the practical use of dibenzyl ketone as a triplet sensitizer. Moreover, the triplet lifetime is less than the singlet lifetime, a most extraordinary situation probably caused by the high rate at which triplet **1** undergoes acyl bond cleavage. 1,3-Cyclohexadiene interacts primarily with the ketone singlet, since quenching of fluorescence is nearly as efficient as quenching of ketone disappearance. The upward curvature in the ketone-disappearance plot for this diene, however, as well as the formation of its photodimers (see below), indicates some triplet energy transfer.

In order to determine whether any decarbonylation occurs from the singlet of **1**, an attempt was made to measure its intersystem crossing yield (Φ_{ic}) by monitoring the isomerization of *cis*-1,3-pentadiene to the trans isomer.[16] Although the results at high quencher concentration left no doubt that isomerization occurred, the fact that the sensitizer disappeared before enough diene had been isomerized to measure accurately and the possibility that isomerization was caused by re-

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(7) T. Kubota, K. Shima, S. Toki, and H. Sakurai, *Chem. Commun.*, 1462 (1969).

(8) F. S. Wettack, G. D. Renkes, M. O. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970).

(9) Based upon a comparison of the integrated fluorescence intensity of 1 in hexane with that of 0.2 *M* acetone (Φ_f = 0.01)[10] under conditions of equal absorbance.

(10) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(11) This measurement was done on a TRW nanosecond flash apparatus in nondegassed solutions using a Corning 7-54 filter on the exciting deuterium lamp.

(12) W. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(13) P. J. Wagner, C. A. Stout, S. Searles, Jr., and G. S. Hammond, *ibid.*, **88**, 1242 (1966); N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesley, *ibid.*, **87**, 2613 (1965); D. I. Schuster, B. R. Sckolnick, and F. H. Lee, *ibid.*, **90**, 1300 (1968).

(14) Values of k_q are uncertain, particularly when the triplet quenching constant is small.[15]

(15) D. I. Schuster, A. C. Fabian, N. P. Kong, W. C. Barringer, W. V. Curran, and D. H. Sussman, *J. Amer. Chem. Soc.*, **90**, 5027 (1968).

(16) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(17) P. S. Engel and B. M. Monroe, *Advan. Photochem.*, in press.

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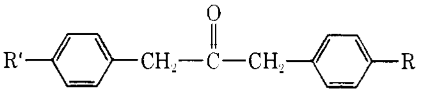
Photodecarbonylation in Solution. I. Quantum Yields and Quenching Results with Dibenzyl Ketones

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]