Mechanisms of Photochemical Reactions in Solution. LVIII.[1] Photoreduction of Camphorquinone[2]

Bruce M. Monroe[3] and Steven A. Weiner

Contribution No. 3714 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.
Received July 15, 1968

Abstract: The photoreduction of camphorquinone (**1**) in methanol and isopropyl alcohol solution has been studied in detail. The products are the isomeric ketols **2** and **3**, plus, in methanol, adducts **4** and **5**. The quantum yields for disappearance of the diketone are 0.018 ± 0.003 in methanol and 0.057 ± 0.006 in isopropyl alcohol. The intermediate semiquinone radical, **7**, has been characterized by electron spin resonance spectrophotometry. The radical appears either to have a symmetrical structure or to oscillate rapidly between two equivalent unsymmetrical structures. The rate of termination for **7** in isopropyl alcohol was found to be $1.6 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. The reaction is sensitized with either *m*-methoxyacetophenone or benzophenone. Reaction in the presence of the former is unexceptional but use of benzophenone results in much increased quantum yields which increase as the concentration of **1** decreases. This anomalous effect is attributed to "chemical sensitization" in which benzophenone ketyl radical, formed by hydrogen abstraction from the solvent, transfers a hydrogen atom to camphorquinone.

The photoreactions of α-diketones have been studied under a variety of reaction conditions since Klinger irradiated an ether solution of benzil in 1886.[4] Irradiation of biacetyl[5] or camphorquinone (**1**)[6] in the presence of oxygen produces a variety of reaction products. Vapor phase photolysis of biacetyl[7] or hexafluorobiacetyl[8] yields products formed by cleavage of the carbon–carbon bond between the two carbonyl groups. However, when α-diketones are irradiated in solution in the presence of a hydrogen donor, the products almost invariably can be rationalized by a mechanistic pathway involving initial hydrogen abstraction by the photoexcited α-diketone followed by further reaction of the resulting radical intermediates. Long-chain and cyclic α-diketones abstract a hydrogen intramolecularly from the γ-carbon to form 1,4-biradicals which close up to produce cyclobutanols.[9] Biacetyl, irradiated in isopropyl alcohol[9a,10] or cyclohexene,[11] gives products derived from initial hydrogen abstraction from the solvent although photoenolization appears to be a major side reaction in aqueous solution[12] and decarbonylation has been reported in solvents with no readily abstractable hydrogens.[13]

The other α-diketones whose photoreactions in oxygen-free solution have been studied are all nonenolizable and cannot readily undergo other intramolecular reaction. Hexafluorobiacetyl is reported to undergo photoreduction when irradiated in hydrocarbon solution or in the vapor state in the presence of a hydrocarbon.[8] Photoreduction takes place when 3,3-dimethylindandione is irradiated in alcohol solution.[14] Benzil yields 1,2,3,4-tetraphenyl-2,3-dihydroxy-1,4-butanedione when irradiated in ether,[4] ethanol,[10,15] or aldehyde[15] solution. In cyclohexane a more complex product mixture is obtained.[16] Irradiation of 1,1,4,4-tetramethyl-2,3-dioxotetralin in a variety of solvents leads primarily to products formed by selective 1,2 addition of a solvent molecule to one carbonyl to give an α-hydroxy ketone and/or to the reduction product, depending on the solvent.[17] Camphorquinone (**1**) gives analogous products when irradiated in *o*- and *p*-xylene[18] and in the presence of aldehydes,[19] but it is reported to be photostable in methanol or isopropyl alcohol in the absence of oxygen.[6]

Because of the reported photostability of camphorquinone in oxygen-free solvents and the availability of the optically active *d* isomer, we attempted to use it as an optically active photosensitizer.[20] In the course of our investigation we have found that **1** undergoes the expected photoreactions in oxygen-free methanol or isopropyl alcohol. A study of the mechanism of this reaction has shown that the triplet state is the photoreactive state. In addition an interesting, symmetrical radical intermediate has been observed and the kinetics of its decay in solution have been studied.

Results and Discussions

Direct Irradiation. Irradiation of an isopropyl alcohol solution of camphorquinone (**1**) under a nitrogen atmosphere or in sealed, degassed tubes gave a mix-

---

[1] Part LVII: G. R. Ziegler, *J. Am. Chem. Soc.*, **91**, 446 (1969).

[2] A preliminary report of this work has appeared: B. M. Monroe, S. A. Weiner, and G. S. Hammond, *ibid.*, **90**, 1913 (1968).

[3] National Institutes of Health Postdoctoral Fellow, 1967–1968.

[4] H. Klinger, *Chem. Ber.*, **19**, 1862 (1886).

[5] D. E. Hoare and G. S. Peterson, *Advan. Photochem.*, **3**, 107 (1964).

[6] J. Meinwald and H. O. Klingele, *J. Am. Chem. Soc.*, **88**, 2071 (1966).

[7] W. A. Noyes, Jr., G. B. Porter, and J. E. Jolly, *Chem. Rev.*, **56**, 49 (1956).

[8] I. M. Whittemore and M. Szwarc, *J. Phys. Chem.*, **67**, 2492 (1963).

[9] (a) W. H. Urry and D. J. Trecker, *J. Am. Chem. Soc.*, **84**, 118 (1962); (b) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, 609 (1962).

[10] W. D. Cohen, *Chem. Weekblad*, **13**, 590 (1916).

[11] P. W. Jolly and P. de Mayo, *Can. J. Chem.*, **42**, 170 (1964).

[12] J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967).

[13] S. A. Greenberg and L. S. Forster, *J. Am. Chem. Soc.*, **83**, 4339 (1961).

[14] C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, **6**, 516 (1941).

[15] G. Ciamician and P. Silver, *Chem. Ber.*, **34**, 1530 (1901); C. W. Porter, H. C. Ramsperger, and C. Steel, *J. Am. Chem. Soc.*, **45**, 1827 (1923); A. Benrath, *J. Prakt. Chem.*, **87**, 416 (1913).

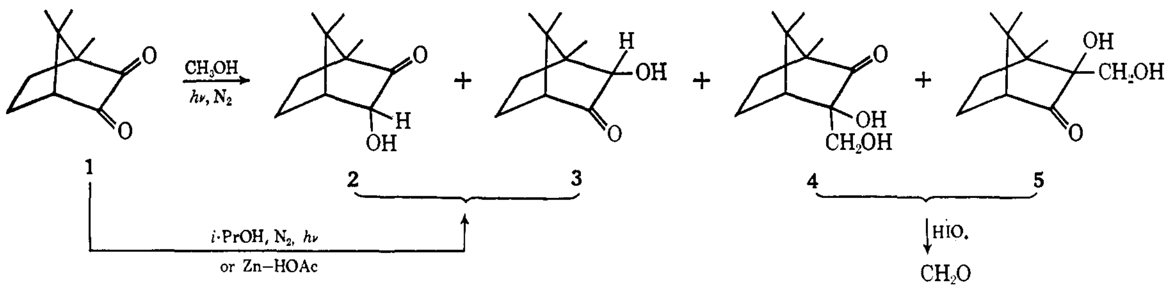
[16] D. L. Bunbury and C. T. Wang, *Can. J. Chem.*, **46**, 1473 (1968).

[17] G. E. Gream, J. C. Paice, and C. C. R. Ramsey, *Australian J. Chem.*, **20**, 1671 (1967).

[18] M. B. Rubin and R. G. La Barge, *J. Org. Chem.*, **31**, 3283 (1966).

[19] M. B. Rubin, R. G. La Barge, and J. M. Ben-Bassat, *Israel J. Chem.*, **5**, 39p (1967).

[20] G. S. Hammond and R. S. Cole, *J. Am. Chem. Soc.*, **87**, 3215 (1965); S. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968).



ture of *endo*-3-hydroxycamphor (**2**) and *endo*-2-hydroxyepicamphor (**3**), the two α-hydroxy ketones formed by reduction of **1** with zinc and acetic acid.[21] It had previously been reported that these products were formed when **1** was irradiated in methanol or isopropyl alcohol in the presence of oxygen but that **1** was photostable when irradiated in a variety of solvents with or without filters in the absence of oxygen.[6] Since the sealed tubes were degassed by four freeze–pump–thaw cycles with pumping to 5 × 10^{-4} mm on each cycle, we believe that no significant amount of oxygen could have been present during irradiation. Although we found that the reduction products were formed on irradiation through quartz or Pyrex, irradiation through a uranium glass filter was used for preparative work since its omission led to the formation of new products with much shorter vapor phase chromatographic retention times during the later stages of the reaction. Although the nature of these products was not investigated, we believe that they are secondary reaction products formed by photoreactions of **2** and **3**. The hydroxy ketones were identified by comparison of the nuclear magnetic resonance and infrared spectra of the mixture with those of a mixture of **2** and **3** prepared by zinc–acetic acid reduction of **1** and by the inseparability of the two mixtures on vapor phase chromatography. The quantum yield for the disappearance of camphorquinone in isopropyl alcohol, measured using 2537-Å light in runs carried to 12% or less conversion, was 0.057 ± 0.006. It was necessary to use 2537-Å exciting light for these determinations because camphorquinone has a relatively low absorbance at 3130 Å ($\epsilon \sim 9$) and practically none ($\epsilon < 1$) at 3660 Å.

Irradiation of **1** in methanol under nitrogen gave a mixture of products containing mostly **2** and **3** plus two new hydroxy ketones and several unidentified minor products. The new hydroxy ketones were thermally unstable, decomposing on injection into the vapor phase chromatograph (injector temperature ~230°) to produce camphorquinone. Infrared and nuclear magnetic resonance spectra are consistent with the assignment of structures **4** and **5** to these compounds. Cleavage with periodic acid yields the expected amount of formaldehyde. Although we have no firm basis for the indicated stereochemistry, it is assigned on mechanistic grounds and by analogy to that of the products obtained by Rubin and La Barge from the irradiation of **1** in xylene.[18] Only a trace of ethylene glycol was present in the reaction mixture. The quantum yield for disappearance of **1** in methanol was 0.018 ± 0.003.

Mechanism of the Reaction. The reaction has every characteristic of a normal photoreduction with the solvent serving as the hydrogen donor.[22] The mechanism shown in eq 1–9 is consistent with all the experimental observations.

$$C \xrightarrow{h\nu} C^1 \qquad (1)$$

$$C^1 \xrightarrow{k_f} C + h\nu \text{ (fluorescence)} \qquad (2)$$

$$C^1 \longrightarrow C \qquad (3)$$

$$C^1 \xrightarrow{k_{is}} C^3 \text{ (intersystem crossing)} \qquad (4)$$

$$C^3 \xrightarrow{k_d} C \qquad (5)$$

$$C^3 + AH_2 \xrightarrow{k_c} CH\cdot + AH\cdot \text{ (abstraction)} \qquad (6)$$

$$AH\cdot + C \xrightarrow{k_2} CH\cdot + A \qquad (7)$$

$$CH\cdot + CH\cdot \xrightarrow{k_t} CH_2 + C \text{ (termination)} \qquad (8)$$

$$CH\cdot + AH\cdot \longrightarrow CHAH \qquad (9)$$

C^1 is camphorquinone singlet, C^3 is camphorquinone triplet, and AH_2 is the solvent. In k_d are included all first-order triplet decay processes.

The hydrogen-transfer step (eq 7) is completely analogous to the hydrogen transfer observed in the photoreduction of benzophenone in isopropyl alcohol.[23] In isopropyl alcohol disproportionation of the camphorquinone radical (eq 8) is the only method of product formation while in other solvents radical coupling (eq 9) is also an important or even the sole termination route. Since all further experiments were done in isopropyl alcohol, the kinetic schemes will consider only termination *via* radical disproportionation except where indicated.

If the quantum yield for intersystem crossing for camphorquinone singlet to its triplet is 1.00, the quantum yield for product formation, which is the same as that for disappearance of **1**, is given by the expression

$$\Phi = \frac{k_c[AH_2]}{k_c[AH_2] + k_d} \qquad (10)$$

Although the quantum yield for intersystem crossing has not been measured for **1**, that of biacetyl is known to be nearly unity.[24] Even though **1** has a weak fluorescence in isopropyl alcohol, fluorescence is probably not a major pathway for the decay of camphorquinone singlet since the quantum yield of fluorescence for biacetyl is only 2.2 × 10^{-3} and that of **1** might be expected to be equally small.[24a]

The triplet nature of the abstracting state was established by sensitization of the reduction with *m*-methoxyacetophenone. This sensitizer was chosen because

---

[21] M. O. Foster and P. Prabhashanker, *J. Chem. Soc.*, 127, 1855 (1925); H. Rupe and F. Müller, *Helv. Chim. Acta*, 24, 265E (1941); I. Fleming and R. B. Woodward, *J. Chem. Soc., C*, 1289 (1968).

[22] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 137–161.

[23] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, 81, 1068 (1959).

[24] (a) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 14, 53 (1960); (b) *ibid.*, 14, 481 (1960).

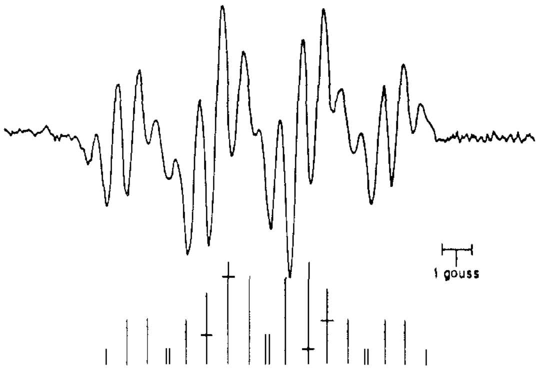


Figure 1. Esr spectrum of radical produced from camphorquinone on irradiation in isopropyl alcohol (top); calculated spectrum based on splitting constants (bottom) given in Table II.

aromatic carbonyl compounds undergo intersystem crossing with high efficiency,[25] its triplet energy (72.4 kcal/mol)[26] is much higher than that of **1** (51.6 kcal/mol),[27] and it has a very low quantum yield for photoreduction in isopropyl alcohol indicating that its triplet state is a poor hydrogen abstractor.[26] The quantum yield for photoreduction was measured under conditions in which more than 85% of the light was absorbed by the sensitizer and the remainder by **1** (Table I). Thus the triplet nature of the reaction is established. An analysis of the kinetic scheme for photosensitized reduction shows that the quantum yield for product formation, which is the same as that for camphorquinone disappearance, is also expressed by eq 10. The close agreement between the direct and sensitized quantum yields of photoreduction indicates that the quantum yield for intersystem crossing for **1** is close to unity.

Table I. Sensitized Photoreduction of **1** with *m*-Methoxyacetophenone

[Camphorquinone], M	[Sensitizer], M	Φ
0.05	2×10^{-3}	0.060 ± 0.003
0.10	2×10^{-3}	0.058 ± 0.003

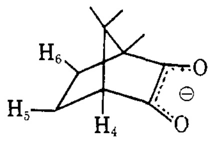
Electron Paramagnetic Resonance

Irradiation of **1** was carried out in the cavity of an electron paramagnetic resonance spectrometer with samples degassed by five freeze–thaw cycles under high vacuum. In methanol solution the signal was of an intensity too low to be resolved. However, in isopropyl alcohol, a species having a spin resonance signal with an easily resolvable hyperfine structure was observed. The spectrum is shown in Figure 1, along with a theoretical reconstruction based on the splitting constants listed in Table II. Symmetrical structure **7** is assigned to the radical because of the simplicity of the spectrum and the good agreement of the splitting constants for **7** with those of camphorquinone semidione (**6**), produced by reduction of **1** with alkali metals.[28] Under our experimental conditions a splitting constant as low as 0.5 G would most likely not have been observed.

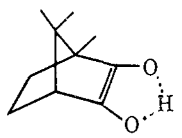
Table II. Coupling Constants of Radicals in Gauss

	A_{CH_3}	A_{H_4}	A_{H_5}	A_{H_6}	$A_{H(endo)}$
6[a]	0.55, 0.15	2.08	3.01	3.01	0.221
7	0.7	2.0	3.4	3.4	

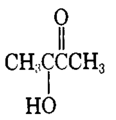
[a] From ref 28.



6



7


$\overset{\displaystyle O}{\overset{\|}{CH_3C}}\underset{\underset{\displaystyle HO}{|}}{C}CH_3$

8

It should be noted that a symmetrical structure has not been observed for the analogous radical derived from biacetyl (**8**). In neutral media the two methyl groups show very different A_{CH_3} values and an additional splitting of 2.07 G, assigned to the hydroxyl hydrogen, is observed.[29,30] While it is possible that the splitting constant assigned to H_4 in the spectrum of **7** is due to the hydroxyl proton, it is unlikely in view of the similarity of the splitting constants for H_5, H_6, and that for one of the methyl groups of **6**. It seems reasonable to propose that these differences stem from the fact that **8** probably has its carbonyl groups in the *trans* configuration while those of **7** are held rigidly *cis*. The simplicity of the hyperfine pattern is compatible with two unsymmetrical structures that interconvert by rapid internal exchange of the hydrogen atom between the two carbonyl positions. This rapid exchange process, which is possible only if the carbonyl groups are *cis*, could explain our failure to observe an interaction of the electron spin with the spin of the hydroxyl hydrogen. The conversion of the spectrum of **8** to a symmetrical splitting pattern showing coupling to six equivalent protons and no coupling to the hydroxyl proton has been observed at pH 0.5.[30] This must be due to exchange of the hydroxyl proton with the solvent *via* protonation to form the conjugate acid of **8** followed by proton loss to re-form **8** without disturbing the *trans* configuration since the value of A_{CH_3} in strong acid is the average of the two observed in neutral media.

Using methods previously described,[31] we were able to measure the termination constant (k_t) for **7**. In isopropyl alcohol this value was 1.6×10^7 M^{-1} sec^{-1} and the steady-state radical concentration was 2×10^{-5} M. Irradiation of benzophenone under the same conditions yielded a value of 1.2×10^8 M^{-1} sec^{-1} for k_t and 2.8×10^{-6} M for the steady-state radical concentration.

We have also examined the effect of acid and base on the steady-state radical concentration in isopropyl alcohol. In the presence of 1.5×10^{-5} N potassium hydroxide, irradiation of 0.01 M camphorquinone yields

---

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

(26) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *J. Am. Chem. Soc.*, **89**, 5466 (1967).

(27) T. R. Evans and P. A. Leermakers, *ibid.*, **89**, 4380 (1967).

(28) G. A. Russell, E. T. Strom, E. R. Talaty, K. Y. Chang, R. D. Stephens, and M. C. Young, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 27, 3 (1966).

(29) H. Jeldes and R. Livingston, *J. Chem. Phys.*, 47, 1465 (1967).

(30) R. J. Prichett, *Mol. Phys.*, 12, 481 (1967).

(31) S. A. Weiner and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 1659 (1968); S. A. Weiner and G. S. Hammond, *ibid.*, in press.

a steady-state radical concentration of 7.8×10^{-5} *M*. In the presence of 10^{-3} *M* sulfuric acid this value is 5.8×10^{-5} *M*. Thus both acid and base increase the steady-state radical concentration by about a factor of 10.[32] However, this concentration of acid has only a slight effect on the quantum yield for disappearance of **1** (~10% increase) while in 1.5×10^{-5} *N* base the quantum yield increases to about 0.14.

Sensitization with Benzophenone. In an attempt to establish the triplet nature of the reaction, initial sensitization experiments were carried out with benzophenone. However, the quantum yield for the disappearance of **1** was much higher than that obtained from direct irradiation and decreased with increasing concentration of **1** (Table III). This phenomenon is caused by two mechanisms of sensitization, "physical sensitization," or energy transfer, and "chemical sensitization," or proton transfer, occurring in the same reaction.[33] Since benzophenone can also abstract a hydrogen atom from isopropyl alcohol, there is competition for the benzophenone triplet between camphorquinone and the solvent. After the benzophenone abstracts a hydrogen atom from the solvent, the benzophenone ketyl radical thus formed can transfer a hydrogen atom to **1** forming **7** and ground-state benzophenone. Such chemical sensitization has recently been observed in the benzophenone-sensitized photoreduction of acridine[35] and the benzophenone- or acetone-sensitized photoreduction of benzophenone imines.[34] The following mechanism indicates the steps in the reaction.

Table III. Benzophenone-Sensitized Reduction of **1** in Isopropyl Alcohol

[**1**], *M*	ϕ_{-1}	[Benzophenone] $\times 10^2$, *M*	λ, Å
0.003	0.386 ± 0.019	2.38	3130
0.005	0.364 ± 0.018	2.38	3130
0.010	0.321 ± 0.016	2.37	3130
0.010	0.319 ± 0.016	2.38	3130
0.020	0.264 ± 0.013	5.07	3660
0.020	0.264 ± 0.013	2.37	3130
0.040	0.181 ± 0.009	4.70	3130
0.050	0.149 ± 0.007	5.10	3130
0.060	0.143 ± 0.006	5.50	3660
0.075	0.119 ± 0.006	5.10	3130
0.100	0.104 ± 0.005	2.38	3130
0.100	0.103 ± 0.005	2.37	3130
0.200	0.087 ± 0.004	5.50	3660

$$\mathrm{B} \xrightarrow{h\nu} \mathrm{B}^1 \longrightarrow \mathrm{B}^3 \tag{11}$$

$$\mathrm{B}^3 + \mathrm{C} \xrightarrow{k_q} \mathrm{C}^3 + \mathrm{B}\ \text{(energy transfer)} \tag{12}$$

$$\mathrm{B}^3 + \mathrm{AH_2} \xrightarrow{k_a} \mathrm{BH}\cdot + \mathrm{AH}\cdot \tag{13}$$

$$\mathrm{BH}\cdot + \mathrm{C} \xrightarrow{k_1} \mathrm{CH}\cdot + \mathrm{B}\ \text{(proton transfer)} \tag{14}$$

$$\mathrm{C}^3 \xrightarrow{k_d} \mathrm{C} \tag{5}$$

$$\mathrm{C}^3 + \mathrm{AH_2} \xrightarrow{k_c} \mathrm{CH}\cdot + \mathrm{AH}\cdot \tag{6}$$

$$\mathrm{AH}\cdot + \mathrm{C} \xrightarrow{k_2} \mathrm{CH}\cdot + \mathrm{A} \tag{7}$$

$$\mathrm{CH}\cdot + \mathrm{CH}\cdot \xrightarrow{k_t} \mathrm{CH_2} + \mathrm{C} \tag{8}$$

B is benzophenone and BH· is the benzophenone ketyl radical

Solution of the steady-state kinetics for ϕ, the quantum yield of product formation, which is the same as the quantum yield of disappearance of **1**, gives

$$\phi = \left(\frac{k_q k_c[\mathrm{C}]}{k_a(k_d + k_c[\mathrm{AH_2}])} + 1\right)\left(\frac{k_a[\mathrm{AH_2}]}{k_q[\mathrm{C}] + k_a[\mathrm{AH_2}]}\right) \tag{15}$$

Substitution of the quantum yield for the disappearance of **1** sensitized by *m*-methoxyacetophenone in isopropyl alcohol and the concentration of isopropyl alcohol in neat solution into eq 10 gives

$$k_d = 205k_c \tag{16}$$

From a study of the naphthalene quenching of benzophenone photoreduction in isopropyl alcohol the ratio of k_q to k_a has been measured.[36] We assume that naphthalene and camphorquinone both quench benzophenone triplet at the same rate because both have triplet excitation energies considerably lower than that of benzophenone. This assumption leads to the following relationship.

$$k_q = 192k_a[\mathrm{AH_2}]\ M^{-1} \tag{17}$$

Substitution of these values for k_d and k_q into eq 15 gives

$$\phi = \frac{11.6[\mathrm{C}] + 1}{192[\mathrm{C}] + 1} \tag{18}$$

The quantum yield of photoreduction as a function of camphorquinone concentration, as predicted by this mechanism, is shown in Figure 2. The points are the experimentally determined values. As the concentration of **1** approaches zero the mechanism predicts that hydrogen abstraction will become the sole reaction of benzophenone triplet. Hence the predicted quantum yield goes to unity at zero concentration of **1**. However, as the concentration of **1** increases, energy transer from benzophenone triplet to **1** increases with a corresponding decrease in hydrogen abstraction by benzophenone triplet. Since the benzophenone triplet is a much more efficient hydrogen abstractor than camphorquinone triplet, the predicted quantum yield decreases, asymptotically approaching 0.06. This is the same value observed on sensitization with *m*-methoxyacetophenone, conditions under which all the sensitizer triplets transfer their energy to **1**.

By appropriate mathematical manipulation eq 15 can be converted to

$$\frac{\phi[\mathrm{C}]}{1 - \phi} = \left(\frac{k_c[\mathrm{AH_2}]}{k_c[\mathrm{AH_2}] + k_d}\right)\left(\frac{[\mathrm{C}]}{1 - \phi}\right) + \frac{k_a[\mathrm{AH_2}]}{k_q} \tag{19}$$

---

(32) We believe that in acid solution we are still observing the neutral radical but that in basic solution we are seeing the radical anion **6**. The similarity of the hyperfine splitting constants for the two radicals prevents a clear-cut differentiation under our experimental conditions.

(33) The term "chemical sensitization" has previously been used to describe a phenomenon of this nature.[34] This term is probably technically incorrect since the term "sensitization" implies energy transfer. This type of behavior might better be called an "induced reaction" by analogy with the induced reactions observed in redox systems. However, we will use the term "chemical sensitization" in this discussion to avoid the introduction of new terminology and because it is a convenient way of looking at this type of mechanism. Energy transfer is described as "physical sensitization" instead of "sensitization" in order to stress the basic dichotomy of mechanism and to prevent confusion with "chemical sensitization."

(34) M. Fischer, *Chem. Ber.*, **100**, 3599 (1967).

(35) E. Van'der Donckt and G. Porter, *J. Chem. Phys.*, **46**, 1173 1967).

(36) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

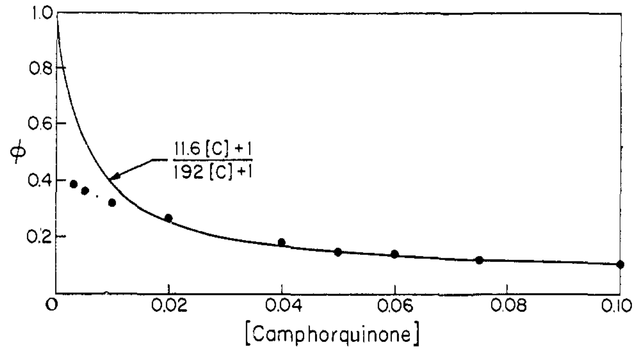


Figure 2. Plot of calculated quantum yield for camphorquinone photoreduction *vs.* concentration. Points are experimental values.

Equation 19 indicates that a plot of $[C]/(1 - \phi)$ against $\phi[C]/(1 - \phi)$ should give a straight line whose slope is the quantum yield measured under conditions of total energy transfer (eq 10) and whose intercept is the ratio of the abstraction constant times the concentration of hydrogen donor to the quenching constant (eq 17). These two parameters whose values, determined from other experiments, were used to convert eq 15 to eq 18 may also be evaluated from the data in Table III. This plot is shown in Figure 3.

Ignoring for the moment the three quantum yield determinations for concentrations of **1** less than 0.02 *M* a least-squares plot through the seven remaining points gives a slope of 0.061 and an intercept of 5.37×10^{-3}. Since the errors are estimated to be about 5%:

$$\phi = 0.061 \pm 0.003 \qquad (20)$$

$$\frac{k_a[AH_2]}{k_q} = 5.37 \times 10^{-3} \qquad (21)$$

or

$$k_q = (186 \pm 9)k_a[AH_2]\ M^{-1} \qquad (22)$$

These values are in excellent agreement with those determined by other methods. Thus it has been demonstrated that the benzophenone-sensitized photoreduction of **1** occurs by a dual sensitization mechanism in which both "physical sensitization," energy transfer from the sensitizer, and "chemical sensitization," proton transfer from the sensitizer ketyl radical, take place simultaneously.

At high concentrations of **1** the experimentally determined quantum yields are in excellent agreement with those predicted by this mechanism. However, at concentrations of **1** less than 0.02 *M* the values are markedly lower than the predicted values. One possible explanation is that the benzophenone ketyl radical is coupling to form benzpinacol instead of transferring to **1** when **1** is present in low concentration. However, no benzpinacol was observed except on prolonged irradiation after the yellow color of **1** had completely disappeared. Measurement of the optical density of irradiated solutions at 3660 Å (where both **1** and benzpinacol are practically transparent and benzophenone has significant absorption) showed no decrease in optical density indicating no change in benzophenone concentration. Further, in a study of the "chemically sensitized" photoreduction of acridine by benzophenone, it was found that at acridine concentrations greater than 5×10^{-5} *M* the disappearance of benzophenone ketyl radical was essentially unimolecular.[35] This indicated that hydrogen atom transfer to acridine rather than benzpinacol formation was taking place at any concentration of acridine greater than 5×10^{-5} *M*.

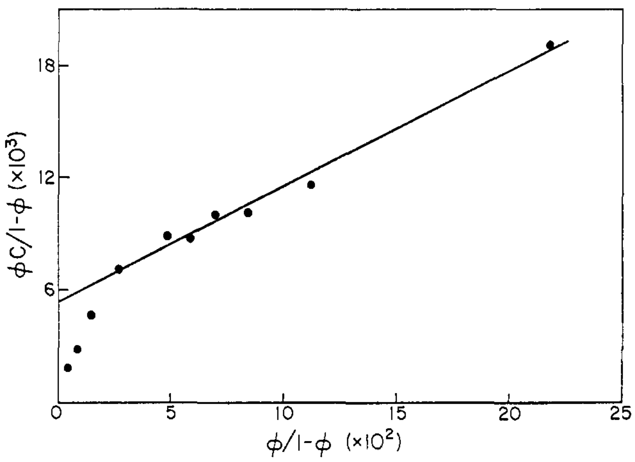


Figure 3. Determination of ϕ and $K_a[AH_2]/K_q$ from eq 19.

As a further test **1** was irradiated in the cavity of the epr spectrometer with light filtered to isolate the 3660-Å region of the spectrum. No signal was observed. However, irradiation of 5.5×10^{-3} *M* benzophenone and 0.01 *M* **1** under these conditions gave a signal, which on partial resolution showed a crude quartet with a line spacing of approximately 3.3 G. No other radical was detected. This suggests that hydrogen atom transfer from the benzophenone ketyl radical (eq 14) is much faster than benzpinacol formation. Irradiation of benzophenone gave a value of $1.2 \times 10^{8}\ M^{-1}\ \text{sec}^{-1}$ for k_{tBH} and 2.8×10^{-6} *M* for the steady-state radical concentration. A lower limit of $k_1 = 70\ M^{-1}\ \text{sec}^{-1}$ is obtained from eq 23 if we assume that an upper limit for the benzophenone ketyl radical concentration in the presence of 0.1 *M* camphorquinone is 2.8×10^{-6} *M*.

$$k_1[BH\cdot][C] \gg 2k_{tBH}[BH\cdot]^2 \qquad (23)$$

$$k_1 \gg \frac{2k_{tBH}[BH\cdot]}{[C]} = 70\ M^{-1}\ \text{sec}^{-1} \qquad (24)$$

In the derivation of this mechanism it was assumed that all the benzophenone triplets either transferred triplet energy to **1** or abstracted a hydrogen atom from the solvent. No provision was made for decay of benzophenone triplet to the ground state. However, it is well known that the quantum yield for benzpinacol formation from the photoreduction of benzophenone in isopropyl alcohol is unity only under ideal conditions.[22,23,36-38] This indicates, that the benzophenone triplet may disappear by routes other than proton abstraction from the solvent. Murov and Yang found that the quantum yield for benzophenone disappearance decreased with increasing light intensity and concluded that, since at higher light intensities there were higher concentrations of radical intermediates, quenching of excited states by these intermediate radicals occurred.[38] In our work higher quantum yields and correspondingly

---

[37] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); S. G. Cohen and W. V. Sherman, *ibid.*, **85**, 1642 (1963); A. C. Testa, *J. Chem. Phys.*, **67**, 1341 (1965); M. J. Gibian, *Tetrahedron Letters*, 5331 (1967).

[38] N. C. Yang and S. L. Murov, *J. Am. Chem. Soc.*, **88**, 2852 (1966).

higher radical concentrations are predicted at lower concentrations of **1** while at higher concentrations lower quantum yields and correspondingly lower radical concentrations are predicted. It seems reasonable that the deviations from the predicted quantum yields at low concentrations of **1** may be due to quenching of excited states by intermediate radicals.

Because of the ease with which benzophenone can induce photoreactions *via* "chemical sensitization," we believe that care should be exercised in the use of sensitization by benzophenone as a criterion for a triplet mechanism, especially for those reactions in which radical intermediates are known or suspected.[34,35,39] As an alternative we suggest the use of those aromatic carbonyl compounds whose triplet states are inefficient hydrogen abstractors yet still have high triplet energies and high quantum yields of triplet formation, such as *m*-methoxyacetophenone ($E_{\mathrm{T}} = 72.4$ kcal/mol), 3,4-methylenedioxyacetophenone ($E_{\mathrm{T}} = 65.8$ kcal/mol), and 2-acetylnaphthalene ($E_{\mathrm{T}} = 59.4$ kcal/mol).[25,26] Further, because of the ease with which **1** can accept a hydrogen atom from the benzophenone ketyl radical (eq 14), the results of quenching experiments with α-diketones such as biacetyl, camphorquinone, or benzil should be interpreted with caution.

Experimental Section

Nuclear magnetic resonance spectra were measured in deuteriochloroform solution with a Varian A-60A nuclear magnetic resonance spectrometer. Shifts are expressed in δ units relative to internal tetramethylsilane. Peak areas are expressed relative to the largest peak in the spectrum. Infrared spectra were determined with a Beckman IR 7 spectrometer. Electron paramagnetic resonance spectra were obtained with a Varian V-4502 spectrometer equipped with a 9-in. magnet with 100-kcps field modulation. Vapor phase chromatographic analysis was carried out with a Loenco Model 70 gas chromatograph with a thermal detector. Optical density determinations were made with a Beckman DU spectrophotometer. Microanalyses were carried out by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

Materials. Eastman *d*-camphorquinone and Aldrich *dl*-camphorquinone were used without further purification. These materials contain somewhat less than 1% camphor. Matheson Coleman and Bell spectroquality reagent isopropyl alcohol and methanol were used for irradiation. Aldrich *m*-methoxyacetophenone was used without further purification. Benzophenone was recrystallized twice from 60–70° ligroin.

Photoreduction in Isopropyl Alcohol. A solution of 2.50 g of *d*-camphorquinone (**1**) in 250 ml of isopropyl alcohol was placed in an immersion-type apparatus and flushed with nitrogen 0.5 hr before irradiation. Irradiation was carried out with a Hanovia 450-W mercury arc lamp equipped with a uranium glass filter. Nitrogen was bubbled through the solution during irradiation. After 52 hr the solvent was evaporated to give 2.53 g of a white solid: $[\alpha]_{\mathrm{D}}$ 11.3 ± 0.2° (*c* 17.1, $CHCl_3$); $\nu_{\max}$ ($CHCl_3$) 3580, 3450, and 1743 cm^{-1}; nmr 5.0 (broad singlet, area 1.1, –OH), 4.24 (doublet, $J = 5$ cps, 0.5, >CHC*H*OHCO–), 3.89 (singlet, 0.5, ⩾CC*H*OHCO–), and 2.4–0.8 (complex multiplet with sharp peaks at 1.06, 1.00, 0.98, 0.93, 0.88, area 14, CH,CH_2, and CH_3). The nuclear magnetic resonance and infrared spectra were identical with those of a mixture of *endo*-3-hydroxycamphor (**2**) and *endo*-2-hydroxyepicamphor (**3**) prepared by the zinc–acetic acid reduction of camphorquinone.[21]

Vapor phase chromatography on a 30% Carbowax column at 210° indicated three peaks. The relative retention times and relative areas were: 0.17 (0.3%), 0.72 (2.0%), and 1.00 (97.7%). The first peak has the same retention time as and is inseparable from camphor, which is present in the starting material. The second peak is camphorquinone. The final peak has the same retention time as and is inseparable from a mixture of **2** and **3**.

If the irradiation was carried out through quartz or Pyrex without the uranium glass filter, in addition to the reduction products at least six new products (relative retention time: 0.008–0.020) began to appear near the end of the run.

The photoreduction was also carried out in sealed, degassed tubes. Aliquots (3 ml) of a solution containing 425 mg of *d*-camphorquinone in 25 ml of isopropyl alcohol were placed in seven constricted 13-mm o.d. Pyrex test tubes. The sample tubes were degassed by four freeze–pump–thaw cycles with pumping to 5×10^{-4} mm in each cycle and sealed with the stopcock open to vacuum. The tubes were taped to a Pyrex immersion well and irradiated by a 450-W Hanovia medium-pressure mercury arc lamp with a uranium glass filter. After 18.5 hr of irradiation the yellow color of camphorquinone had disappeared. Five of the tubes were opened, and the combined solution was evaporated to give 250 mg of white solid. This solid was inseparable by vpc from a mixture of **2** and **3**.

Photoreduction in Methanol. A solution of 2.70 g of *d*-camphorquinone in 250 ml of methanol was irradiated as above. After 44 hr of irradiation the light yellow solution was evaporated to give 2.94 g of yellow oil. The optical density at 4680 Å of a solution of this oil in isopropyl alcohol showed that less than 3% of unreacted **1** remained. However, vapor phase chromatography indicated a 3:1 mixture of ketones **2** and **3** and unreacted **1** plus smaller amounts of other products.

Column chromatography of 2.60 g of this mixture was carried out on 130 g of silica gel. Elution with 10% ether in petroleum ether gave 250 mg of **1**. Elution with 45–60% ether gave 1.44 g of a mixture of **2** and **3**. Elution with 80% ether gave 368 mg of a colorless oil (**4** and **5**) which was purified by a short-path vacuum distillation in a semimicro sublimer. The distillate had the following properties: $\nu_{\max}$ ($CHCl_3$) (sh), 3590, 1740, 1398, and 1380 cm^{-1}; nmr; broad peak at 3.53 with a sharp singlet at 3.70 (total area 4, >C(O*H*)C*H*$_2$O*H*), 2.36–1.30 (complex multiplet, 5, -CH-CH_2CH_2–), and 1.41, 1.01, and 0.93 (sharp singlets, total area 9, -CH_3). The broad peak at δ 3.53 disappears when the sample is shaken with D_2O to leave the sharp singlet (relative area 1.90).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.74; H, 9.15. Found: C, 66.64; H, 9.14.

Periodic Acid Cleavage of 4 and 5. The oil eluted by 80% ether (**4** and **5**) was cleaved with periodic acid and the formaldehyde analyzed by the chromotropic acid procedure.[40] Because of the water insolubility of the mixture, methanol was used as the solvent for the mixture and the standards. Cleavage of 84.3 mg of material produced 0.446 mmol of formaldehyde (calcd 0.425 mmol).

Direct Irradiation Quantum Yield Determination. The following general procedure was followed for direct irradiation quantum yield determination. A solution of camphorquinone was prepared by the addition of a weighed amount of camphorquinone to a volumetric flask and dilution to the mark with solvent; 2 ml of this solution was diluted to 10 ml and the optical density at 4680 Å measured (ϵ_{CQ} 38.5, isopropyl alcohol). Aliquots (3 ml) were transferred with a syringe to 13-mm o.d. quartz tubes which were attached to Pyrex constrictions *via* graded seals. The sample tubes were degassed by three freeze–pump–thaw cycles with pumping to 5×10^{-4} min in each cycle and sealed off with the stopcock open to vacuum. All tubes were stored in the dark before and after irradiation.

The sample tubes were irradiated on a "merry-go-round" apparatus which ensured equal light intensity to every sample. A 450-W Hanovia medium-pressure mercury arc lamp was employed as a light source. Since **1** has low absorption at 3130 Å ($\epsilon \sim 9$) and 3660 Å ($\epsilon < 1$), the quantum yield was measured using 2537-Å light ($\epsilon \sim 50$). The 250-mm region of the spectrum was isolated by a single solution of about 2-cm path length containing 450 g of nickel sulfate hexahydrate, 300 g of cobaltous sulfate heptahydrate, and 0.175 g of 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene perchlorate (K & K Laboratories) made up to 1 l. with distilled water. Due to decomposition it was necessary to replace the filter solution with fresh solution during a run. Light intensity was determined by ferrioxalate actinometry.[41] The concentrations

---

(39) J. E. Hodgkins and J. A. King, *J. Am. Chem. Soc.*, **85**, 2679 (1963); R. W. Binkley, *J. Org. Chem.*, **33**, 2311 (1968); H. Labhart, *Angew. Chem. Intern. Ed. Engl.*, **6**, 812 (1967).

(40) J. C. Speck, Jr., in "Methods in Carbohydrate Chemistry," Vol. I, R. L. Whistler and M. L. Wolfrom, Ed., Academic Press, New York, N. Y., 1962, pp 441–445.

(41) C. A. Parker, *Proc. Roy. Soc.* (London), **A220**, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, **A235**, 518 (1956). The exact procedure used is described in H. L. Hyndman, Ph.D. Thesis, California Institute of Technology, 1968.

were such that both the sample and actinometer solutions had an optical density of >2 for a 1-cm path length. Since the "merry-go-round" is designed so that light is incident only upon a 2-cm^2 area of the sample tube at its widest point, greater than 99% of the incident light was absorbed by both the sample and actinometer.

Sample tubes were removed at various times during the initial 2–12% of reaction. The disappearance of **1** was measured by the decrease in optical density at 4680 Å. The quantum yield for camphorquinone disappearance was calculated for each tube and the product of quantum yield times for each tube was plotted against time to give a straight line whose slope, the quantum yield, was determined by a least-squares analysis. This treatment of the data corrects for possible errors in determination of the initial optical density of the solution and is equivalent to a plot of moles of reaction *via* Einsteins of light added.

In the determination of the quantum yield for the disappearance of **1** in methanol all operations were carried out under a red light due to the ease with which **1** undergoes photooxidation in methanol.

Photosensitized Quantum Yield Determinations. The following general procedure was used for the photosensitized quantum yield determinations. A weighed amount of **1** was added to a volumetric flask, a volume of a stock solution of sensitizer added, and the flask filled to the mark with solvent. The initial optical density was measured at 4680 Å. If necessary the sample was diluted to obtain an optical density of less than 0.8. Three or four milliliter aliquots were transferred to 13-mm o.d. Pyrex test tubes whose upper portions had been constructed. These were degassed and sealed as above.

The sample tubes were irradiated on a "merry-go-round" apparatus using a 450-W Hanovia medium-pressure mercury vapor arc lamp as a light source. At the concentration of sensitizer used >99% of the light was absorbed by the sample. In the benzophenone-sensitized experiments the 313-mμ region of the spectrum was isolated by a two-compartment filter consisting of a 1.5-cm path length of an aqueous solution of 26 g of cobaltous sulfate heptahydrate per 100 ml and a 0.6-cm path length of 0.132 g of potassium chromate in 250 ml of 1% aqueous sodium carbonate. In the *m*-methoxyacetophenone-sensitized experiments this region was isolated by a two-part filter consisting of the potassium chromate filter solution which was recirculated through the quartz immersion well and a Corning 7-54 glass filter. The 366-mμ region of the spectrum was isolated by a filter made up of a Corning 0-52 and a Corning 7-37 glass filter. Sample tubes were removed over the first 2–20% of reaction and analyzed as above. The determinations with 3130-Å light were corrected for camphorquinone absorption and for the amount of reaction occurring from this absorption.

Electron Paramagnetic Resonance. Sample tubes were degassed by three freeze–pump–thaw cycles with a forepump followed by two such cycles with a diffusion pump with pumping 3×10^{-6} mm Hg on the final cycle and sealed off. Irradiation was carried out by a Hanovia 2500-W mercury–xenon high-pressure mercury vapor lamp. The light was filtered through 10 cm of 2% cobalt chloride solution and focused on a $^3/_8$-in. hole in a copper plate which was used as the cover plate for the esr cavity. To isolate the 3660-Å region of the spectrum a Corning 7-37 filter immersed in a Pyrex beaker of water was also placed in the light path. Steady-state radical concentrations and decay constants were obtained by methods that have previously been described.[31]

Acknowledgments. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479. We wish to thank Dr. Steven Murov for fruitful discussions. We are also grateful to Professor George S. Hammond for discussion and provision of research facilities.

Photochemical Transformations of Small Ring Carbonyl Compounds. XIX. The Photochemistry of Benzoylcyclobutanes[1-3]

Albert Padwa,[4] Edward Alexander, and Mark Niemcyzk[5]

Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214.
Received August 6, 1968

Abstract: The photolysis in benzene of cyclobutyl phenyl ketone has been found to afford four products. The structures have been assigned as 1-phenyl-4-penten-1-one, 2-hydroxy-2-phenylbicyclo[1.1.1]pentane, cyclobutylphenylcarbinol, and the pinacol of starting material. The formation of the keto olefin and the bicyclopentanol is considered to proceed through a diradical intermediate formed by transannular hydrogen abstraction by the excited n–π^* triplet. The inefficiency of the photoreaction, both in terms of quantum yield and rate, is attributed to the unfavorable geometry required for internal hydrogen transfer. *cis-* and *trans*-2-phenylcyclobutyl phenyl ketones undergo rapid photointerconversion followed by a further intramolecular reaction to produce 1,5-diphenyl-4-penten-1-one. The photoisomerization has been rationalized by homolytic ring cleavage of the cyclobutyl ring.

The photochemical behavior of three-ring carbonyl compounds has been the subject of extensive study.[6] Although much remains to be learned about the electronic configuration of the excited state, there has emerged a fair understanding of the potential reactivity of this class of compounds.[7] In the case of conjugated cyclopropyl ketones, the primary photochemical process often involves ring opening by breakage of the cyclopropyl bond that conjugates best

---

[1] For part XVIII, see A. Padwa and R. Gruber, *J. Am. Chem. Soc.*, 90, 4456 (1968).

[2] Support of this work by a grant from the National Science Foundation (Grant GP-9385) is acknowledged with appreciation.

[3] This work was presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P88.

[4] Alfred P. Sloan Foundation Research Fellow, 1968–1970.

[5] National Science Foundation Undergraduate Research Participant, summer 1967.

[6] For a review see A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 92.

[7] (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, pp 377–427; (b) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 71–93.