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.

* Address correspondence to this author at: Analytical and Information Division, Esso Research and Engineering Co., Linden, N. J. 07036.

W. K. Robbins,* R. H. Eastman
Department of Chemistry, Stanford University,
Stanford California 94305

Received May 19, 1970

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

Sir:

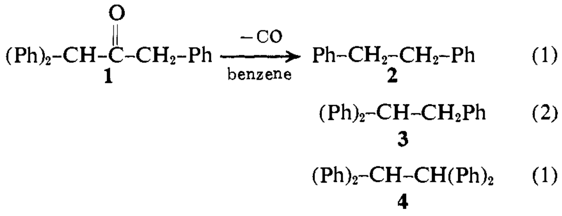
We have previously shown[1] that dibenzyl ketones photodecarbonylate in solution with high quantum efficiency *via* an extremely short-lived triplet state. In this communication, we will present evidence for a stepwise mechanism for this process.

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-

---

(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).



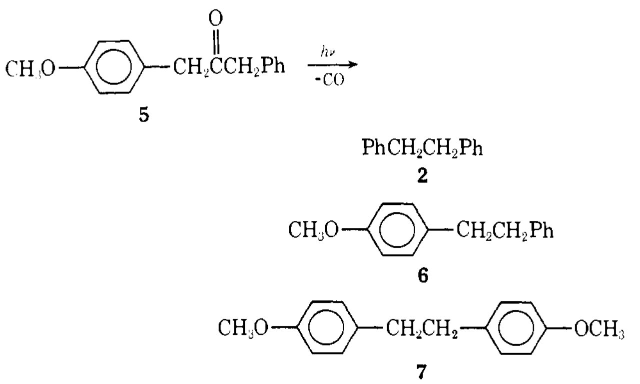
$$\underset{1}{(Ph)_2\text{-}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}Ph} \xrightarrow[\text{benzene}]{-CO} \underset{2}{Ph\text{-}CH_2\text{-}CH_2\text{-}Ph} \quad (1)$$

$$\underset{3}{(Ph)_2\text{-}CH\text{-}CH_2Ph} \quad (2)$$

$$\underset{4}{(Ph)_2\text{-}CH\text{-}CH(Ph)_2} \quad (1)$$

decarbonylation in solution.[2b] The latter mechanism has been frequently[3] proposed for such a process, but without any empirical support. We have employed two methods which give evidence supporting the stepwise mechanism.

First, 1-(4-methoxyphenyl)-3-phenyl-2-propanone (**5**) was photolyzed[1] in solvents of differing viscosities.



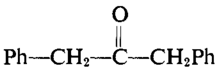
As can be seen in Table I, the distribution of product ethanes **2**, **6**, and **7** was unaffected over a nearly 100-fold viscosity range. This requires that the loss of carbon monoxide occur in such a manner that the two alkyl radicals generated from the photoexcited ketone arise with a significant separation. Thus, there is no evidence of "cage combination" in the product formation such as that frequently found in concerted processes.[4] However, since these viscosity changes have no effect on the total quantum yield, the initial α cleavage(s) must occur with an excess of energy sufficient to destroy the "cage" produced by the solvents used in this study.

Table I. The Effect of Solvent Viscosity on the Quantum Yields of Products in the Photolysis[a] of 1-(4-Methoxyphenyl)-3-phenyl-2-propanone (**1**)

Solvent	Viscosity, cps at 30°[b]	Φ_{sym} (2, 6)[c]	Φ_{unsym} (7)[c]	Φ_{tot}[d]
Benzene	0.56	0.12	0.24	0.48
Cyclohexane	0.80	0.12	0.25	0.49
Decane	0.80	0.12	0.27	0.51
Ethanol	1.00	0.08	0.16	0.32
2-Propanol	1.77	0.13	0.26	0.52
2-Methyl-2-propanol	3.32	0.11	0.22	0.44
Cyclohexanol	41.1	0.09	0.22	0.40

[a] Duplicate, degassed 3-ml aliquots of 0.05 *M* ketone **1** irradiated at 313 nm for 30 min. [b] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Vol. 1, Elsevier, New York, N. Y., 1950; Vol. II, 1965. [c] Product values determined *via* glpc relative to a hexadecane internal standard, ±20%. [d] Calculated as $2(\Phi_{sym}) + \Phi_{unsym}$.

On this basis it was felt that if the decarbonylation were stepwise, then it might be possible to trap the phenylacetyl radical. With this objective, dibenzyl ketone (**8**) was irradiated[1] in the presence of several

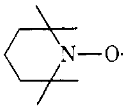


$$Ph\text{—}CH_2\text{—}\overset{O}{\overset{\|}{C}}\text{—}CH_2Ph$$

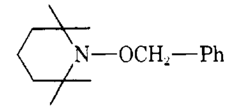
8

concentrations of tri-*n*-butyltin hydride.[5] However, even employing the hydride as solvent (3.4 *M*) the only *photo*product observed was toluene. Since tri-*n*-butyltin hydride donates its hydrogen with a bimolecular rate constant[5-7] of 10^6 l. mol^{-1} sec^{-1}, the phenylacetyl radical must decarbonylate at least an order of magnitude faster.

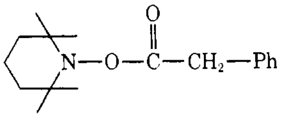
In order to take advantage of the diffusion-controlled trapping rate (theoretically[9] 10^{10} l. mol^{-1} sec^{-1}) expected for radical combination, the nitroxide 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (**9**) was used



9

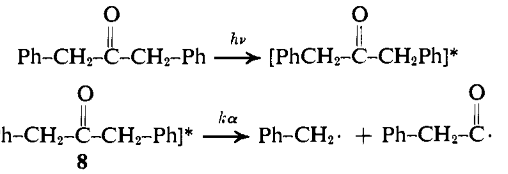


10



11

to try to trap the phenylacetyl radical. This compound (**9**) was selected because it is simple[10] to prepare and has a low extinction coefficient (ϵ 14) at the irradiating wavelength (313 nm). When a benzene solution containing a 1:1.9 molar ratio of the ketone **8** and nitroxide **9** was photolyzed to completion, a 3:2 ratio of the benzyl ether **10** and the phenyl acetate **11** was formed.[11,12] The formation of the latter compound proves[13] that the photodecarbonylation procedes *via* a two-step mechanism involving the formation of the phenylacetyl radical exclusive of a solvent cage.



$$Ph\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}Ph \xrightarrow{h\nu} [PhCH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2Ph]^*$$

$$\underset{8}{[Ph\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}Ph]^*} \xrightarrow{k\alpha} Ph\text{-}CH_2\cdot + Ph\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\cdot$$

---

(3) (a) J. S. Swenton, *J. Chem. Educ.*, **46**, 217 (1969); (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967.

(4) (a) S. F. Nelson and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1965); (b) S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

(5) G. S. Hammond and P. A. Leermakers, *ibid.*, **84**, 207 (1962).

(6) D. J. Carlson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

(7) Kuivila[8] has reported the thermal trapping of the triphenylacetyl radical with tri-*n*-butyltin hydride; however, under his conditions, a free-radical mechanism may not have been operative.

(8) H. G. Kuivila and E. J. Walsh, *J. Amer. Chem. Soc.*, **88**, 571 (1966).

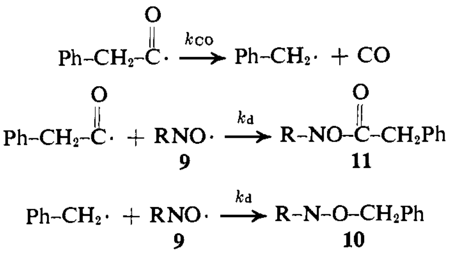
(9) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 627.

(10) (a) W. L. Hubbell, Stanford University, private communications; (b) R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, **32**, 3273 (1965).

(11) Both new compounds gave correct elemental analyses and their spectral data were consistent with the given structures.

(12) The product ratio was determined on the basis of the integrated nmr peak area for the benzylic hydrogens as determined directly on the crude photolyzate.

(13) No spectral evidence (ir, uv, or esr) for any ground-state interaction of the nitroxide **9** and ketone **8** was found. When an equimolar mixture of these compounds was photolyzed to completion, the three products **2**, **10**, and **11** were found to account for 87% of the ketone and 80% of the nitroxide.



$$\mathrm{Ph{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}\cdot \xrightarrow{k_{CO}} Ph{-}CH_2\cdot + CO}$$

$$\mathrm{Ph{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}\cdot + \underset{\mathbf{9}}{RNO\cdot} \xrightarrow{k_d} \underset{\mathbf{11}}{R{-}NO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2Ph}}$$

$$\mathrm{Ph{-}CH_2\cdot + \underset{\mathbf{9}}{RNO\cdot} \xrightarrow{k_d} \underset{\mathbf{10}}{R{-}N{-}O{-}CH_2Ph}}$$

By application of the steady-state approximation and several simplifying assumptions to this mechanism, it is possible to derive the following expression

$$\frac{[\mathrm{R{-}NO{-}CH_2Ph}]}{[\mathrm{R{-}N{-}O{-}C({=}O){-}CH_2{-}Ph}]} = \frac{2k_{\mathrm{CO}}}{k_{\mathrm{d}}[\mathrm{NO}\cdot]_0/2} + 1$$

Substituting the values found in this study, one calculates k_{CO} to be of the order of 10^8 sec^{-1}.

It is gratifying to note that this value is consistent with the failure of the tri-*n*-butyltin hydride to trap the phenylacetyl radical ($k_{\mathrm{H}}[\mathrm{Bu_3SnH}] = 10^6$ sec^{-1}). Furthermore, since unimolecular *radical* reactions usually proceed at the same rate in nonpolar solvents and in the vapor phase,[14] the value for phenylacetyl radical decarbonylation calculated here may be compared with that found for the acetyl radical at room temperature in the vapor phase[15] ($k_{\mathrm{CO}} \simeq 1$ sec^{-1}). Thus, one α-phenyl substitution increases the rate of decarbonylation by a factor of 10^8. This rate difference (10^8) corresponds to a ΔE_{a} which nearly matches the current benzyl resonance energy of $\sim$12.5 kcal/mol.[16]

As a result of these studies, we are confident that the photodecarbonylation of dibenzyl ketones in solution occurs *via* a two-step mechanism which is independent of cage effects.

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.

---

[14] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

[15] J. A. Kerr and J. G. Calvert, *J. Phys. Chem.*, **69**, 1022 (1965).

[16] R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 651 (1966).

* Address correspondence to this author at: Analytical and Information Division, Esso Research and Engineering Co., Linden, N. J. 07036.

W. K. Robbins,* R. H. Eastman
Department of Chemistry, Stanford University
Stanford, California 94305

Received May 19, 1970

The Thermal Fragmentation of Cyclohexanone[1]

Sir:

Recently there has been interest expressed in parallels in the mechanism of fragmentation of molecules when induced, respectively, by light or electron impact.[2] In the case of cyclohexanone both photochemical (Norrish type I) and electron-impact fission take place in the α position.[3] Such thermolytic work as has been previously reported[4] suggested that this, too, involved α cleavage. We describe here evidence which indicates that the major pathway for thermolysis involves β cleavage.

The thermolyses were conducted in a flow system at 1050°,[4] and gave the following products: methyl vinyl ketone[6,7] (MVK, 25), ethylene (85), ethane (3), acetylene (5), propylene (16), allene (7), 1-butene (7),

Table I. Deuterium Distributions for Ethylene, Isoprene, and Methyl Vinyl Ketone from Pyrolysis of Specifically Labeled Cyclohexanones and Methylenecyclohexane[a]

	Cyclohexanone, %	Ethylene, %	Methyl vinyl ketone, %
α deuterated[b,f]	d_1 0.2	d_0 4.5	d_0 0.3
	d_2 0.6	d_1 9.9	d_1 1.0
	d_3 8.0	d_2 22.6	d_3 3.4
	d_4 91.2	d_3 1.8	d_3 25.7
		d_4 1.2	d_4 69.6
	3.90 atoms of D/molecule	0.65 atom of D/molecule	3.63 atoms of D/molecule
β deuterated[c,f]	d_0 0.1	d_0 7.4	d_0 2.4
	d_1 1.1	d_1 23.8	d_1 21.4
	d_2 8.0	d_2 64.3	d_2 75.0
	d_3 28.9	d_3 4.5	d_3 1.2
	d_4 61.8		
	3.51 atoms of D/molecule	1.66 atoms of D/molecule	1.75 atoms of D/molecule
γ deuterated[d,f]	d_0 49.8	d_0 68.5	d_0 99.2
	d_1 50.2	d_1 31.5	d_1 0.8
	0.50 atom of D/molecule	0.32 atom of D/molecule	0.008 atom of D/molecule

	Methylenecyclohexane-d_4, %	Ethylene, %	Isoprene, %
α deuterated[e,f]	d_0 0.1	d_0 58.7	d_0 0.6
	d_1 0.4	d_1 13.7	d_1 1.6
	d_2 0.2	d_2 21.4	d_2 9.6
	d_3 5.1	d_3 4.9	d_3 31.8
	d_4 87.1	d_4 1.3	d_4 47.9
	d_5 6.1		d_5 7.4
	d_6 1.1		d_6 1.1
	4.02 atoms of D/molecule	0.76 atom of D/molecule	3.51 atoms of D/molecule

[a] Average of duplicate runs. [b] The recovered cyclohexanone had 3.82 atoms of D/molecule distributed as follows: d_0, 0.0; d_1, 0.9; d_2, 1.7; d_3, 12.8; d_4, 84.7. This indicates a minor amount of equilibration. [c] Recovered, 3.50 atoms of D/molecule. [d] Recovered, 0.5 atom of D/molecule. [e] Recovered, 4.00 atoms of D/molecule. [f] Distribution essentially unchanged from starting material.

---

[1] (a) Flash Thermolysis. Part IV. (b) This work was supported by the Petroleum Research Fund administered by the American Chemical Society.

[2] Photochemical Cleavage: R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963); R. G. Shortridge and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 2228 (1970), and references therein cited. Mass Spectrometric Cleavage: H. Budziekiewicz, C. Djerassi, and D. H. Williams in "The Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 19.

[3] C. D. Hurd, H. Greengard, and A. S. Roe, *J. Amer. Chem. Soc.*, **61**, 3359 (1939); E. Ibuki, *Nippon Kagaku Zasshi*, 71, 96 (1950); *Chem. Abstr.*, **45**, 7025 (1950).

[4] The flow system consisted of a heated empty ceramic tube leading to a liquid nitrogen cold-finger.[5] The thermolyses were carried out at 60 μ with calculated contact times of about 10 msec. The technique follows that pioneered for mass spectrometry over the last decade by F. P. Lossing (see, for instance, R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 3204 (1961)) and developed by Hedaya for isolation purposes (see E. Hedaya and D. McNeil, *ibid.*, **89**, 4213 (1967)).

[5] J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, in press. A similar apparatus has been described by E. Hedaya, *Accounts Chem. Res.*, **2**, 367 (1969).

[6] Mole per cent yield based on decomposed cyclohexanone. The products were identified by retention time on gas–liquid chromatography and by mass spectra.

[7] Dr. E. Hedaya (Union Carbide Research Institute) informs us that he has also observed the formation of methyl vinyl ketone from the thermolysis of cyclohexanone.