

PHOTOCHEMISTRY OF 2,2-DIMETHOXY-2-PHENYLACETOPHENONE-
 TRIPLET DETECTION VIA "SPIN MEMORY"

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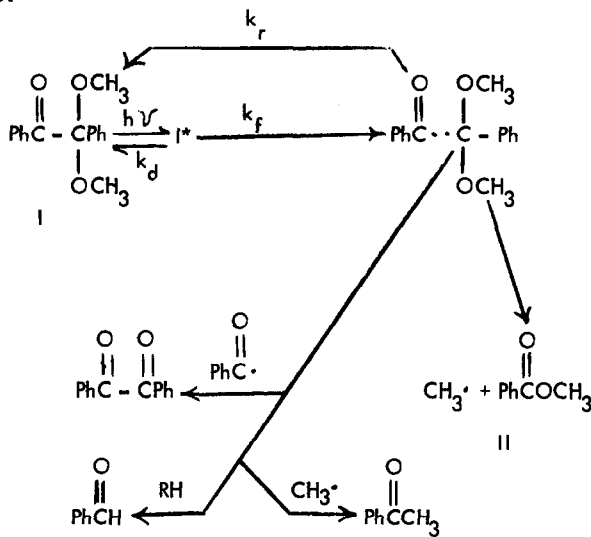
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The photochemistry of α -alkoxyacetophenones has been investigated in some detail. Substitution of the α -carbon with hydrogen or alkyl-substituents leads to Norrish Type II elimination and cyclization upon irradiation,¹ while aryl substitution alters the photochemical course of the reaction to yield Norrish Type I products via α -cleavage.² We now wish to report our results on the photochemistry of the structurally related α -ketoketal, 2,2-dimethoxy-2-phenylacetophenone.³

Irradiation⁴ of I in a variety of solvents resulted in α -cleavage as the sole reaction path. The major products formed were methyl benzoate, II (45-61% yield), resulting from α -cleavage of the initially formed α , α -dimethoxybenzyl radical,⁵ benzaldehyde, benzil, and acetophenone.⁶ Control experiments established that no inter-conversion of primary photoproducts occurred as a result of "dark" reactions or under the irradiation conditions employed in the absence of light. The conversion of I was somewhat faster in aprotic solvents (benzene, and acetonitrile) than in protic media (t-butyl alcohol and 2-propanol).⁷ The ratios of products produced to I consumed in various solvents are presented below:

Mol Ratio	Solvent			
	C ₆ H ₆	CH ₃ CN	(CH ₃) ₃ COH	(CH ₃) ₂ CHOH
Rel. Rate (-I)	1.0	0.97	0.71	0.76
II/-I	0.52	0.45	0.61	0.59
PhCHO/-I	0.19	0.17	0.20	0.25
PhCOCOPh/-	0.09	0.071	0.11	0.067
PhCOCH ₃ /-I	0.048	0.018	0.077	0.0085

While production of benzaldehyde and benzil was relatively constant in "inert" solvents, irradiation of I in a hydrogen donating solvent, 2-propanol, resulted in increased benzaldehyde formation at the expense of benzil and acetophenone. No evidence for hydrogen abstraction by I was found. This is in contrast to the behavior exhibited by aryl-t-alkylketones where carbinol formation is observed.⁹ Increased acetophenone formation with increasing solvent viscosity most likely involved in-cage or near-cage combination of methyl and benzoyl radicals.¹⁰



Various concentrations of I were irradiated in *t*-butyl alcohol solution and the molar ratios, product/II, were determined. The results (see below), show that a proportionately greater amount of acetophenone was produced in dilute solution, where cage effects are most pronounced, while benzaldehyde formation was correspondingly decreased. Benzil formation remained relatively constant, an observation consistent with out-of-cage coupling of two relatively selective benzoyl radicals where diffusive encounter is more significant.

Mol Ratio	Solutions of I, [M] in <i>t</i> -Butyl Alcohol			
	0.15	0.10	0.05	0.01
PhCHO/II	0.24	0.24	0.22	0.18
$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{PhC}-\text{CPh} \end{array}$ /II	0.14	0.13	0.15	0.15
$\begin{array}{c} \text{O} \\ \\ \text{PhC}-\text{CH}_2 \end{array}$ /II	0.085	0.10	0.12	0.14

Photolysis of benzene solutions of I (0.01M) was sensitized with xanthone (E_T , 74 kcal/mol), acetophenone (E_T , 73.6 kcal/mol) and benzophenone (E_T , 69.1 kcal/mol).¹² The relative efficiencies were essentially the same as those of the unsensitized photolysis of I.¹³ Attempts to quench the disappearance of I (0.10M in benzene) with naphthalene (E_T , 60.9 kcal/mol, 0.001M) or isoprene (E_T , 60 kcal/mol, 0.10M)¹⁴ were unsuccessful. The evidence above indicates that unsensitized photolysis of I proceeds via a relatively short-lived triplet state or from an upper singlet state equal in reactivity to the triplet state.

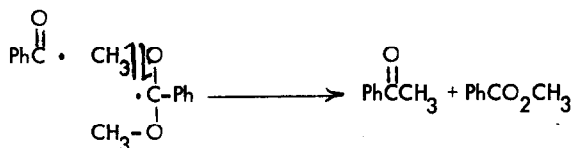
Further information concerning the multiplicity of the reactive state of I was obtained by a study of the effect of quenchers on acetophenone formation. Ferric acetylacetonate, $\text{Fe}(\text{AA})_3$, has been shown to be a very efficient paramagnetic quencher.^{8, 15} Irradiation of I (0.10M in benzene) in the presence of $\text{Fe}(\text{AA})_3$ ($5 \times 10^{-4}\text{M}$) resulted in greater than a six-fold increase in the amount of acetophenone produced without producing any significant change in the rate of disappearance of I. Similar treatment I in the presence of ethyl iodide (0.56M) did not alter efficiency or other product ratios and actually decreased acetophenone, presumably by reaction with the intermediate radicals. Ethyl iodide has been shown to facilitate intersystem crossing.¹⁶ If upper singlets of I were involved, an increase in efficiency or change in product distribution would be expected.

Quencher, [M]	Mol Ratio			
	PhCO_2Me	PhCHO	PhCOCOPh	PhCOCH_3
	-1	-1	-1	-1
None	0.45	0.14	0.091	0.036
$\text{Fe}(\text{AA})_3, [5 \times 10^{-4}]$	0.50	0.079	0.106	0.263

Since $\text{Fe}(\text{AA})_3$ is inert under the irradiation conditions, increased acetophenone formation in its presence can be viewed as a result of increased efficiency of benzoyl and methyl radical combination. Recent evidence has indicated that spin inversion in a caged radical pair may be fast relative to diffusive cage destruction.¹⁷ This requires that $\text{Fe}(\text{AA})_3$ encounter the radicals at or near the site of their generation while their "spin memory" is retained. The initial species must be paramagnetic (triplet) in nature since $\text{Fe}(\text{AA})_3$ would not be expected to significantly affect spin-paired species. This requires that initial α -cleavage of I proceed from the triplet state. Since none of the quenchers employed quenched the disappearance of I, the maximum triplet lifetime of I may be estimated on the order $\tau_{\text{max}} \sim 10^{-6}$ sec and $k\alpha_{\text{min}} \sim 10^{-6}$ sec⁻¹.¹⁸ The data above lead us to conclude that photolysis of 2,2-dimethoxy-2-phenylacetophenone proceeds from a short-lived triplet state, evidenced by the novel effect of a paramagnetic quencher on a secondary radical combination reaction.

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6. Products were identified by glc comparisons with authentic materials and by m/e ratios obtained from a coupled glc-mass spec. arrangement.
7. Estimates of the quantum yields for the disappearance of I (0.1M solutions) were made using comparative irradiations of benzophenone/benzhydrol solutions.⁸ The quantum yield values estimated for the disappearance of I were in the range 0.15 - to - 0.25 for all of the solvents investigated. These values as well as the product ratios were determined at conversions of 50-70% and were corrected for absorption by products. The rate of appearance of products was essentially constant over the irradiation period.
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has not been categorized as typical of the benzoyl radical;¹¹ however, such a process if it occurs could account for a portion of the acetophenone formed. The above route would not be expected to contribute to the enhanced acetophenone formation observed in the presence of a paramagnetic quencher, vide infra.

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18. Values are estimated assuming a value of $k_q \sim \times 10^9$ for the quenchers employed.