Photochemistry of vicinal triketones

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Abstract

Vicinal triketones are converted to the corresponding diketones by irradiation in the presence of electron donors such as 1,4-diazabicyclo[2.2.2]octane (DABCO) or hydroquinone dimethyl ether. The primary step is suggested to be electron transfer to the excited state of trione. Irradiation of triketones alone in toluene, p-xylene, cyclohexane or benzene solutions proceeds with very low quantum yields in the absence of oxygen to give complex mixtures of products. Gas chromatography–mass spectrometry (GC–MS) studies of reactions of diphenyl triketone (1) in p-xylene show that benzaldehyde, p-methylbenzyl phenyl ketone, p,p'-dimethylbibenzyl and products derived from reaction with the traces of oxygen present are formed. Analogous results were observed with di-tert-butyl triketone. The suggested primary photochemical processes are initial α-cleavage of excited trione or hydrogen atom abstraction from the solvent. The equilibrium constant for the hydration of 1 in dioxan at 25 °C is 27.

Keywords: Triketones; Triones; Photolysis; Electron transfer; H-Abstraction; α-Cleavage

1. Introduction

The preparation of the first vicinal triketone, 1,3-diphenylpropane-1,2,3-trione (1, diphenyl triketone), was reported in 1890 by Neufville and von Pechmann [1]; a considerable number of open-chain and cyclic compounds of this type have been reported in the literature since then (for a general review of the chemistry of vic-polyketones, see Ref. [2]). These are of interest for a number of reasons [2]. The rich photochemistry of α-diketones [3] has not been extended to studies of their tricarbonyl analogues. Except for a very brief paper by Schönberg and Mustafa [4], reporting that 1 is converted into benzil by sunlight, and a preliminary communication by Urry et al. [5], demonstrating that dialkyl triketones in the gas phase undergo inefficient α-cleavage followed by radical chain reactions, the photochemistry of such systems remains unexplored (the related ketodiester, diethyl mesoxalate, exhibits normal carbonyl photoreactivity [6]). In this paper, we report an investigation of the photochemistry of a number of vic-triketones.

A major difficulty in working with these compounds is their marked tendency to form hydrates. These are assumed to result from the addition of water to the highly reactive central carbonyl group of vic-trione (e.g. 1→2, Fig. 1). Dihydrates and hemihydrates have also been reported in a number of cases; the latter have been suggested to have structures such as 3. Triketones incorporating bulky end groups, such as mesityl or tert-butyl, show a much lower tendency to undergo hydration. Reported cases of triketone photochemistry, e.g. ninhydrin (5 hydrate) [7], involve photocleavage of the C–OH bond in the hydrate (or in hemiketals) and, while interesting in themselves, are not relevant to trione photochemistry. The study of triones thus requires special drying techniques and carefully dried solvents; the use of most alcohols or other protic solvents is
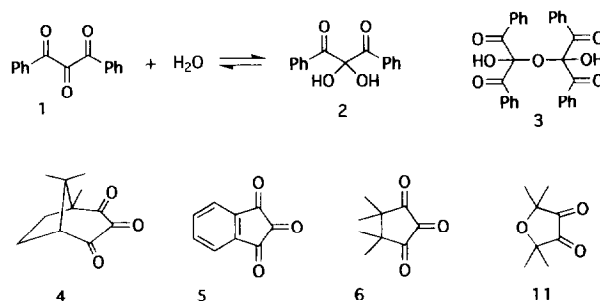

Fig. 1. Formulae of compounds observed.

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precluded. Synthetic procedures for preparing trike-tones often give the hydrates, but free triketone can be obtained by sublimation in vacuum, by drying over phosphorus pentoxide in vacuum, or other methods. Horner and Maurer [8] have shown that reproducible absorption maxima and extinction coefficients can be obtained in methylene chloride solutions containing phosphorus pentoxide. We made a preliminary study of the hydration behaviour in order to define the conditions required for working with trione and not its hydrate. By a combination of gas chromatographic analysis for total water content [9] and visible spectroscopy for analysis of free triketone, it was possible to determine the equilibrium constants for the hydration of diphenyl triketone $(1 + H_2O \rightleftharpoons 2)$ in dioxan at 15, 25 and 35 °C; the values obtained for K_{eq} were 52, 27 and 17 M^{-1} respectively. The triketone hydrate was not stable at higher temperatures (this instability may be due to the occurrence of a benzilic acid-type rearrangement of the oxy anions formed from the hydrate [10]).

With water concentrations no greater than the triketone concentration, the half-lives for the hydration of 1 were of the order of a few hours. These results indicate that, at room temperature, it is possible to obtain qualitative information on the reactions of trione using reasonable care to exclude moisture; quantitative measurements require special precautions. Selective irradiation of trione in the presence of hydrate is possible due to the long-wavelength absorption of triones.

2. Absorption spectra

The absorption spectra of diaryl triones were studied in detail by Horner and Maurer [8] as noted above. They showed that such compounds have absorption maxima in the visible in the range 440–460 nm as well as absorptions at shorter wavelengths. Compound 1 is typical with λ_{max} (CH_2Cl_2) values of 254sh (12 700), 273 (14 700), 290sh (10 000), 350sh (175), 450 (45) nm [8]. The generalization developed more than 40 years ago by Leonard and Mader [11] that the long-wavelength $(n_+ \pi^*)$ absorption maxima of α-diketones vary as a function of the torsion angle between the carbonyl groups (maximum values for angles of 0° or 180°) also appears to apply to triketones, although no systematic study has been reported. Thus, in contrast with the open-chain triones, bicyclic trione 4 has $\lambda_{max} = 550$ nm [8], the long- wavelength maximum of the trione 5 derived from the dehydration of ninhydrin [8] is observed at about 610 nm, and 4,4,5,5-tetramethylcyclopenta-netrione (6, the most planar of these molecules) is a greenish blue substance [12] with $\lambda_{max} = 685$ nm. The structures of a number of triones have been determined by X-ray crystallography; in addition, the structure of

diphenyl triketone in the gas phase has been established by electron diffraction [13]. Attempts to obtain emission spectra were not successful in our and other laboratories.

3. Experimental details

Diaryl triketone hydrates and di-tert-butyl triketone were prepared from the corresponding diaroylmethanes by conversion to diazo compounds followed by reaction with freshly prepared tert-butyl hypochlorite [14]. Crystallization of the hydrate of 1 from ligroin (boiling point (b.p.), 100–110 °C) afforded the free trione. 1,8,8-Trimethylbicyclo[3.2.1]octan-2,3,4-trione hydrate was prepared [15] from camphorquinone and sublimated at 70 °C and 1 mm vacuum to obtain the free triketone 4. Reagent grade solvents were distilled and the samples were boiled to about 75% of their original volume immediately before use to ensure dryness.

Gas chromatography–mass spectrometry (GC–MS) analyses were performed with a Finnigan MAT ITS40 apparatus using a 30 m capillary column coated with GB5.

3.1. Irradiations

The appropriate dark reactions were performed in all cases using UV–visible spectroscopy to monitor any changes. Small-scale photoirradiations were performed with Osram 200 W (Wild–Heerbrugg housing) and 500 W (Oriel housing) high- pressure mercury vapour lamps and 150 W (PTI housing) xenon lamps. Preparative scale irradiations were performed using a General Electric AH/6 water-cooled (Pyrex jacket) 1000 W high-pressure mercury lamp. Samples were degassed by the freeze–pump–thaw technique for quantum yield determinations and for irradiation followed by GC–MS analysis; preparative runs were performed in a nitrogen atmosphere after bubbling solutions with dry nitrogen for 30 min.

3.2. Quantum yields

Samples for quantum yield measurements were prepared as follows. A solution of trione was allowed to stand over a small amount of phosphorus pentoxide for about 30 min, followed by filtration under nitrogen pressure into a Pyrex or quartz cuvette. The absorption spectrum was measured and the process was repeated until no further increase in the long-wavelength maximum was observed. The solutions were then degassed by five freeze–pump–thaw cycles to a vacuum of 1 μm or less and the spectrum was determined after 24 h to show that no change had occurred; samples which showed significant spectral changes were discarded. Irradiations were performed using Osram 200 W mer-

cury vapour lamps (HBO 200) in a Wild–Heerbrugg housing. The 313 nm mercury line was isolated using a combination of a 5 cm layer of nickel(II) sulphate (0.178 M), a 5 cm layer of potassium chromate (0.0005 M) and a Corning CS-7-54 filter. The 436 nm line was isolated using a Schott interference filter. The actinometer was potassium ferrioxalate [16]. Isosbestic behaviour was not observed.

3.3. Preparative irradiation of 1 in p-xylene solution

A solution of triketone (250 mg) in freshly boiled p-xylene (40 ml) in a cylindrical Pyrex cell (diameter, 6 cm) was degassed by bubbling with nitrogen and irradiated for 19 h with unfiltered light from a 1000 W mercury lamp so that about 90% of the starting material was consumed (based on the decrease in the absorption maximum at 450 nm). Chromatography on Florisil afforded p,p'-dimethylbibenzyl (8 mg) and p-methylbenzyl phenyl ketone (40 mg); the identities were established by comparison with authentic samples.

3.4. Irradiation of triones in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO)

A solution of 1 (10 mg, 0.042 mM) and DABCO (5 mg, 0.045 mM) in dry benzene (3 ml) in a 1 cm square Pyrex cell was degassed by four freeze–pump–thaw cycles and sealed. After 3 h of irradiation with unfiltered light from an Osram 200 W lamp, the absorption of the starting material at 450 nm had almost completely disappeared and a new maximum was observed at 365 nm. GC–MS analysis showed a single new peak corresponding to benzil. The benzene solution was chromatographed on silica gel (0.5 g) (4:1 hexane–ether) to give a yellow solid identical in all respects with benzil. A similar experiment with 4 (10 mg) afforded camphorquinone (4 mg).

4. Results and discussion

As noted above, 1 has been reported to afford benzil on exposure of benzene solutions to Cairo sunlight in a CO_2 atmosphere. However, after exposure of a degassed benzene solution to Haifa sunlight for 1 month, only 50% of the starting material had reacted and the product did not contain a measurable amount of benzil. Reaction was faster when degassing was omitted; the product was a complex mixture which contained a small amount of benzil. Further experiments were conducted with mercury vapour lamps.

Decarbonylation to benzil occurred when irradiation was performed in the presence of electron donors. Irradiation of a mixture of 1 and DABCO in benzene solution proceeded slowly, but with the formation of

a single product, benzil, as shown by changes in the UV–visible spectrum, GC–MS analysis and isolation of benzil by column chromatography. Similarly, the cyclic triketone 4 yielded camphorquinone when irradiated in the presence of DABCO. The use of p-dimethoxybenzene instead of DABCO with 1 resulted in a slower reaction (about one-half of the rate observed with DABCO), but the results were the same: the formation of benzil as the only product. The irradiation of a mixture of benzil and DABCO in benzene solution under the same reaction conditions did not result in any reaction (the photoreduction of benzil has been reported to occur on laser irradiation in the presence of triethylamine [17]; electron transfer has been proposed as the primary step).

As shown in Scheme 1, the following mechanism can be suggested to account for these results. Electron transfer from DABCO to the excited state of 1 produces the anion radical of 1 (one resonance form shown), which can form the anion radical (7) of the cyclopropanone. Loss of carbon monoxide (either photochemically and/or thermally) from 7 gives the anion radical of benzil. The sequence is terminated by electron transfer to DABCO cation radical (or to a molecule of 1; such a process would give rise to a chain mechanism which is not consistent with the observed results) to give benzil and regenerate a molecule of DABCO. The observation of benzil as the only reaction product implies that the electron transfer process is faster than other reactions of excited 1. Electron transfer processes are known to be readily reversible, thus accounting for the low overall efficiency of the reaction.

The behaviour of triones in the absence of electron donors proved to be much more complex. Quantum yield measurements were performed using the decrease in the absorption maximum at 450 nm for the calculation of the concentration changes of 1. Details of the preparation of samples for these measurements are described in Section 3.2. The results are summarized in Table 1. It should be noted that very little difference was observed between the reactions in benzene and in the hydrogen-atom-donating solvent p-xylene, excitation at 313 nm into the shorter wavelength band resulted in somewhat higher quantum yields, and there was a small increase in the quantum yields in the presence of oxygen. Similar low quantum yields were observed for the p,p'-
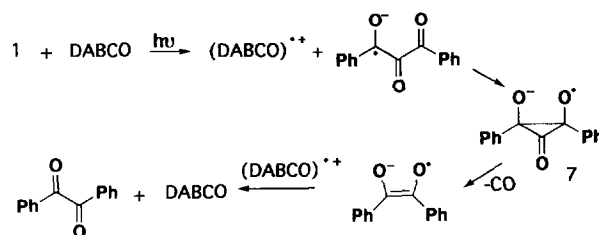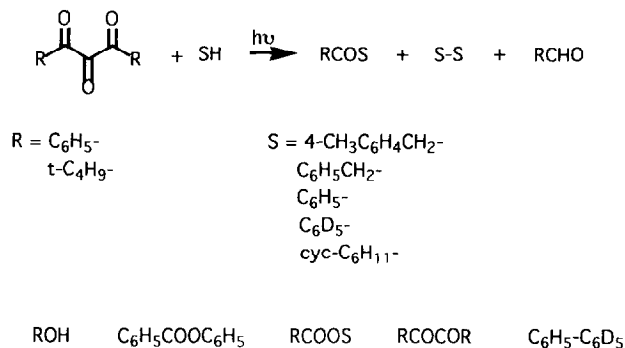

Scheme 1. Electron transfer mechanism for reaction of 1.

Table 1
Quantum yields for reaction of diphenyl triketone (1)

λ_{irr} (nm)	[Trione] (M)	O_2	$\phi^a \times 10^4$ Benzene	p-Xylene
436	0.056	$-$ [b]	3 ± 1	3 ± 1
436	0.056	$+$ [c]	2 ± 1	3 ± 0.5
313	0.0072	$-$ [b]	23 ± 3	40 ± 10
313	0.0072	$+$ [c]	150 ± 30	140 ± 30

[a] Quantum yield for the disappearance of diphenyl triketone in benzene or xylene solutions.
[b] Freeze–pump–thaw degassed.
[c] Air-saturated solution.

$$ R-\overset{O}{\underset{}{C}}-\overset{O}{\underset{O}{C}}-\overset{O}{\underset{}{C}}-R + SH \xrightarrow{h\upsilon} RCOS + S-S + RCHO $$

R = C_6H_5- S = $4-CH_3C_6H_4CH_2-$
t-C_4H_9- $C_6H_5CH_2-$
                                    C_6H_5-
                                    C_6D_5-
                                    cyc-$C_6H_{11}-$

ROH $C_6H_5COOC_6H_5$ RCOOS   RCOCOR $C_6H_5-C_6D_5$

Scheme 2. Photolysis of 1 in various solvents.

disubstituted (Cl, CH_3, CH_3O) derivatives of 1 and for the cyclic triketone 4. These low values made it impractical to study the effects of a variation in the experimental conditions on the quantum yield.

The low quantum yield for the reaction of 1 also made preparative experiments difficult. In one such experiment, a p-xylene solution containing 250 mg of 1 in a Pyrex vessel was irradiated under nitrogen for 19 h with unfiltered light from a 1000 W high-pressure mercury vapour lamp to 90% disappearance of the starting material. (The very low quantum yields of these reactions necessitated the use of a broad spectrum of light such that absorption by ketonic products could occur. The possibility that secondary photoreactions are involved cannot be completely ruled out.) Two products were isolated in low yields from the chromatography of the resulting mixture: a trace of p,p'-dimethylbibenzyl and about 10% of p-methylbenzyl phenyl ketone (p'-methyldesoxybenzoin). GC–MS analysis allowed the identification of the following additional products in yields approximately equal to that of p,p'-dimethylbibenzyl: benzaldehyde, p-methylbenzyl alcohol, p-tolualdehyde, phenyl benzoate, p-methylbenzyl benzoate and benzil. These and the products of the other reactions of 1 are summarized in Scheme 2. Whether benzil is actually a photoreaction product is unclear since traces of benzil were observed in gas chromatographic analyses of pure samples of triketone,

presumably resulting from the thermal decomposition of 1 in the injector block. The presence of traces of oxygen is presumed to be responsible for the esters and alcohols formed.

GC–MS analyses were also performed on products of the irradiation of 1 in toluene, cyclohexane, benzene and hexadeuteriobenzene as summarized in Scheme 2. The results obtained in toluene solution paralleled the results in p-xylene, although the origin of phenyl groups lacking the p-methyl label is ambiguous. Irradiation in cyclohexane gave bicyclohexyl, cyclohexanol, benzaldehyde, phenyl cyclohexyl ketone, cyclohexyl benzoate and benzil (cf. above). The products detected in benzene solution were biphenyl, benzaldehyde and phenyl benzoate; the biphenyl obtained from the reaction of 1 in C_6D_6 was $C_{12}H_5D_5$ as shown by mass spectroscopic analysis. Neither cycloaddition product(s) nor product(s) of abstraction of an allylic hydrogen atom were observed when 1 was irradiated in benzene solution containing tetramethylethylene, in contrast with the results observed with α-diketones.

Results analogous to those observed with 1 were obtained with di-tert-butyl triketone in toluene solution. Products included bibenzyl, trimethylacetaldehyde and tert-butyl benzyl ketone. In addition, a peak was observed with a mass spectrum corresponding to an addition product of toluene and triketone. No di-tert-butyl diketone was detected in these experiments.

The products formed in all of these reactions can be rationalized by assuming: (a) the formation of benzoyl radicals, (b) the formation of a radical resulting from the abstraction of a hydrogen atom from the solvent, and (c) the presence of traces of oxygen which were not removed by the degassing procedures. The solvent-derived radical may be formed in the primary photochemical reaction or by the reaction of benzoyl radicals with the solvent. At least two mechanisms, summarized in Scheme 3, which satisfy these requirements can be considered: initial α-cleavage of trione and/or hydrogen atom abstraction from the solvent by excited trione.

The α-cleavage mechanism results in the cleavage of 1 to benzoyl and phenylglyoxalyl radicals; the latter would decarbonylate rapidly to form a second benzoyl radical. The coupling of two benzoyl radicals leads to benzil, while hydrogen abstraction from the solvent affords benzaldehyde and the radical derived from the solvent (benzyl, p-methylbenzyl, cyclohexyl, phenyl; the formation of pentadeuteriobiphenyl suggests the possible intermediacy of phenyl radicals which add to the solvent hexadeuteriobenzene to produce, after oxidation, the mixed biphenyl; for similar observations in the reactions of α-diketones in benzene solution, see Refs. [3,18]). The coupling of benzoyl and solvent-derived radicals affords the bibenzyls or bicyclohexyl observed. The reactions of the intermediate radicals

α-Cleavage Mechanism

Hydrogen Abstraction Mechanism
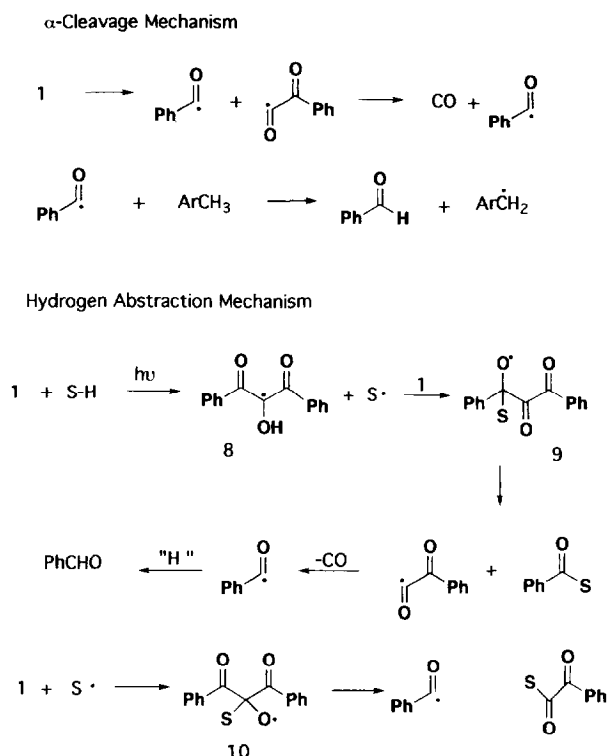
Scheme 3. Mechanisms for the photochemical reaction of 1.

with oxygen account for the remaining products. Possible radical chain reactions are discussed below.

The hydrogen atom abstraction mechanism is based on the well-known propensity of monoketones and diketones to abstract hydrogen from almost any solvent [3]. This leads to the formation of a semitrione radical (8) and a solvent-derived radical. The addition of the solvent radical to ground state 1 yields radical 9, which can undergo fragmentation followed by decarbonylation to give a ketonic product and a benzoyl radical. A reasonable alternative to the formation of 9 is the addition of a solvent-derived radical to the central carbonyl group of 1, as has been suggested in the photolysis of dialkyl triketones [6], resulting in the formation of radical 10. Fragmentation of 10 leads to a benzoyl radical and the species SCOCOPH (not observed). These addition–fragmentation mechanisms result in radical chain reactions which are not consistent with the low quantum yields observed. Furthermore, when 1 was irradiated in the presence of an excess of p-anisaldehyde, no phenyl p-anisyl triketone could be detected in the crude product mixture. The similarity between the quantum yields of the reactions of 1 in p-xylene and benzene is also not consistent with such a mechanism, although it might be rationalized by the assumption of the reversibility of the hydrogen abstraction reaction

At present, we are unable to exclude either of the two mechanistic proposals. It should be emphasized that we are dealing with minor reactions; the quantum

yield for the disappearance of 1 is of the order of 1×10^{-4} and the quantum yield for any single product is 10% or less of that value. A variety of tests which would be reasonable in a better behaved system were not practical. For example, the determination of the quantum yields in perdeuteriotoluene or hexadeuteriobenzene for comparison with those measured in the protio solvents could have provided information on the isotope effects in hydrogen atom abstraction. Such experiments gave results which were within the relatively large experimental errors involved in the determination of such low quantum yields. The same consideration applies to quenching experiments. The absence of detectable emission closed other avenues of mechanistic investigation.

An analogy with the behaviour of α-diketones is not helpful. Although intermolecular and intramolecular hydrogen atom abstractions by the triplet states of α-diketones are well-documented reactions, limited kinetic studies have shown that the rate constants for intramolecular reactions are significantly lower than for the analogous reactions of monoketones. This has been attributed [19] to the appreciably lower energy of the triplet states of diketones compared with monoketones. We can assume that the energies of the excited states of triones will be even lower than those of diketones, so that the rates of hydrogen abstraction by photoexcited triones may be so low that this process is not observed. However, 2,2,5,5-tetramethyltetrahydrofurandione (11) exhibited normal diketone photochemistry [20] in reactions with benzhydrol, toluene, p-xylene, cyclopentene and cyclohexene. This compound has $\lambda_{max} = 559$ nm, a significantly longer wavelength than observed with 1 or the related triones, and may also have a lower triplet energy. The analogy with diketones also suggests that the α-cleavage of excited triketones may be a very slow reaction. Although α-cleavage of biacetyl has been observed in the gas phase, this process has not been found to occur in the solution photochemistry of benzil [21] or any other diketone.

The extremely low photoreactivity of the triketones studied in this work remains puzzling. We considered the possibility that there might be some chemical deactivation pathway, e.g. the formation of a cyclic zwitterion 12 (one resonance form shown) which undergoes rapid reversal to the starting compound (Scheme 4). This possibility was tested by performing irradiations at low temperatures, where 12 (or any other transient intermediate) might be thermally stable. No thermally reversible spectroscopic change was observed on irradiation of 1 in methylcyclohexane at a number of temperatures between $+20$ and $-170\,^{\circ}\text{C}$, thus providing no support for the formation of such an intermediate.

There remains the possibility that an initial photochemical reaction, such as α-cleavage, is reversible in the solvent cage which is an intrinsic part of solution
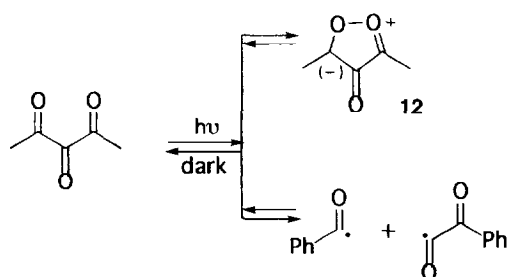
Scheme 4. Possible deactivation paths for triketones.

photochemistry (see Scheme 4). Should such a reversible reaction be involved, it would have to be a rapid reaction with a reversion lifetime faster than 1 μs, as demonstrated by laser-induced optoacoustic studies. The laser-energy-normalized amount of heat evolved by a solution of 1 in cyclohexane on excitation with pulses of 308 nm was identical with that delivered by a solution of 2-hydroxybenzophenone of similar absorbance. The latter compound was taken as a calorimetric reference since it transforms all the absorbed energy into heat within 1 μs, the heat integration time of the experiment. Thus any intermediate responsible for the high yield of internal conversion in 1 should have a lifetime shorter than 1 μs in cyclohexane [22,23].

5. Conclusions

In summary, we have observed that open-chain (and one cyclic) vic-triketones exhibit efficient radiationless deactivation pathway(s) and no competing reaction channel which leads to photochemical reaction with appreciable efficiency. However, the presence of electron donors, such as DABCO, results in electron transfer to give a reactive anion radical which produces the appropriate diketone with the loss of a molecule of carbon monoxide.

Acknowledgments

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