The photocycloaddition of methoxynaphthalenes with acetylacetone and acid-catalysed retardation: reactions of non-fluorescent exciplexes

Yuan L. Chow, Gonzalo E. Buono-Core, Li-Ming Zhang and Carl I. Johansson
Department of Chemistry, Simon Fraser University, Burnaby, BC, Canada, V5A 1S6

Photolysis of either 1- or 2-methoxynaphthalene (MeONp) in the presence of acetylacetone (AA) in acetonitrile and methanol leads to cycloaddition–ring opening to afford acetylacetonylnaphthalene derivatives regioselectively that may undergo the elimination of methanol. The quantum yields of MeONp disappearance (Φ_c) were retarded drastically by H_2SO_4 in the 0.001 mol dm^{-3} range, whereas MeONp fluorescence spectra were hardly affected under the acidic range. As singlet excited 2MeONp is known to lack interaction with H_2SO_4, the photocycloaddition of 2MeONp was used as a model to search for the intermediate responsible for the acid catalysis. Using 'extended fluorescence quenching analysis', the non-fluorescent exciplex of singlet excited 2MeONp and AA is shown, by the oxygen perturbation technique, to be formed reversibly, and to interact with H_2SO_4 promoting to ground state preferentially.

Introduction

Naphthalene derivatives exhibit a wide range of absorption–fluorescence properties and photoreactions that have been reviewed,[1,2] in which exciplex formation and reactions occupy eminent positions. Among them 1-methoxy- and 2-methoxynaphthalene (1MeONp and 2MeONp) have been studied with respect to their excited state reactions.[3–6] In 1986,[7] when we discovered the photocycloaddition of MeONp with acetylacetone (AA) to be a reasonably efficient photoprocess, we faced uncertainty on the interpretation of mechanisms owing to the overlapping absorption of the substrates. However, the photoreaction undoubtedly occurred from the singlet state and, thus, does not share a common mechanism with the de Mayo reaction where triplet excited AA is the reacting species.[8–11] It is also a new insight to the behaviour of excited-state naphthalenes since, so far, enones are known to interact with naphthalenes primarily by energy transfer.[12] Subsequently, it was discovered that a small amount of H_2SO_4 could retard the reaction. In view of the positive catalytic effect of acids on the analogous photocycloaddition of methyl 2-naphthoate,[13,14] it is imperative to investigate the mechanism of the negative acid effects in the MeONp photoreaction. Fortunately we have just established a technique[15] of 'extended fluorescence quenching analysis' (EFQ) that can unravel a transparent (*e.g.*, non-fluorescent) exciplex.[14] We report the application of this method to identify transparent exciplexes as the transient responsible for the observed acid retardation in the photocycloaddition.

The pattern of photocycloaddition

The absorption spectra of methoxynaphthalenes (MeONp) are shown in Fig. 1, and the pertinent data, together with other electronic spectral properties,[16] are summarized in Table 1. Irradiation of 2MeONp with an excess amount of acetylacetone (AA) in acetonitrile (or methanol) under nitrogen rapidly caused the consumption of 2MeONp to form a single product of 1-acetyl-2-acetonylnaphthalene (**3**); this product was assumed to be formed through a [2 + 2] photocycloaddition to **2** followed by elimination of methanol as shown by **1** ⟶ **2** ⟶ **3** in Scheme 1, although **2** was not detected by GC–MS examinations. Compound **3** was readily cyclized by acid treatment in methanol to give phenanthrene derivatives **4a** and **4b**. Similar photolysis of 1MeONp with an excess of AA was slower and gave a more complex mixture as shown by GC monitors; *cis*-1-methoxy-3-acetonyl-4-acetyl-3,4-dihydronaphthalene (**5**) and 1-acetonyl-2-acetylnaphthalene (**7**) were the major products isolated (Scheme 1). During the silicic acid chromatography, fractions containing **7** were always contaminated by a third compound, which showed a strong peak at $M^+ = 258$ (GC–MS) and intense IR absorption at 1266 and 1730 cm^{-1} (GC–FTIR); in repeated chromatography, this compound disappeared to give **7**. This was assumed to be **6** where the elimination of methanol gives **7**; this process was obviously slower than that of **2**. The quantum yields of conversion (Φ_c) and the formation of **3**, at [2MeONp] = 0.01 mol dm^{-3} and [AA] = 0.1 mol dm^{-3}, were 0.029 and 0.021, respectively, in acetonitrile and 0.020 and 0.011 in methanol, respectively (Table 2). Under similar conditions, 1MeONp gave the quantum yield of conversion (Φ_c) of 0.027 and 0.020 in acetonitrile and methanol, respectively. The quantum yield of conversion was reduced to 80% in dioxane and 25% in cyclohexane, respectively, with that in methanol as the reference.

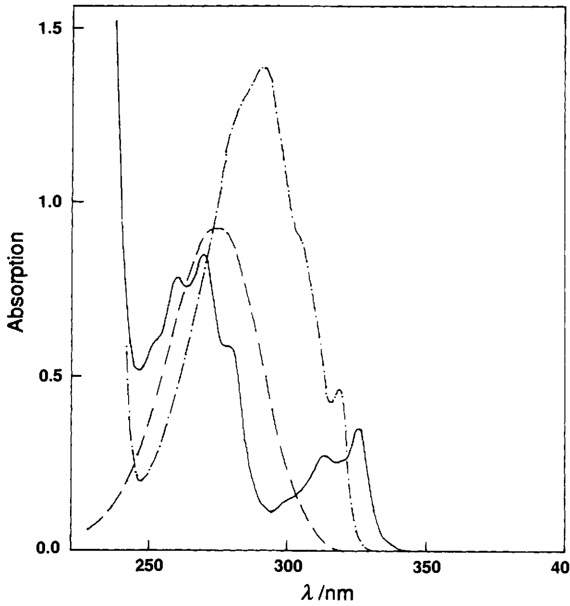
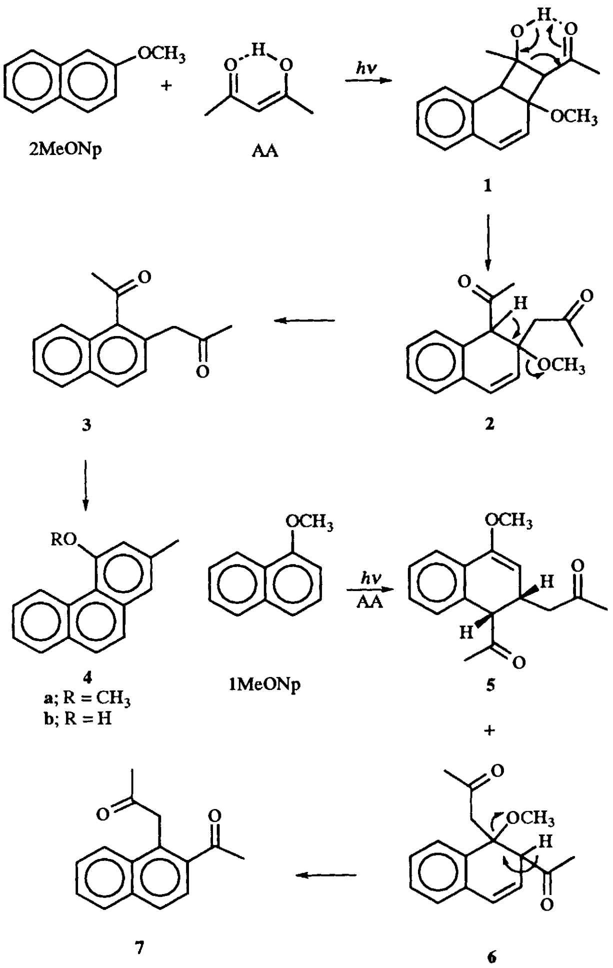


Fig. 1 Absorption spectra of 1MeONp (2.6 × 10^{-4} mol dm^{-3}; – · –), 2MeONp (2.4 × 10^{-4} mol dm^{-3}; ——) and AA (5.4 × 10^{-5} mol dm^{-3}; – –) in methanol

Table 1 Optical characteristics of methoxynaphthalenes (MeONp)[a]

	1MeONp	2MeONp
Absorption λ_{max}/nm (ε)	325 (2400), 319 (1780)[b]	327 (1900), 312 (1090), 326 (1430)[b]
Fluorescence (λ_{em})	340, 352,[b] 354[c]	346, 348,[b] 351[c]
Singlet excited state energy; E_s/kcal mol^{-1}	89 (320 nm)	87 (330 nm)
Triplet excited state energy; E_T/kcal mol^{-1}	60 (479 nm)[d]	60 (479 nm)[d]
Fluorescence lifetimeτ_e°/ns	12.6[e]	14.4,[f] 13.6[b,f]

[a] Unless stated otherwise, the data were measured in acetonitrile. [b] In methanol. [c] In cyclohexane. [d] The spectrum was taken in EPA glass at 77 K. [e] $CH_3CN:H_2O$ = 80:20, τ_e° by time resolved fluorescence decay. [f] Measured by oxygen quenching.



Scheme 1

Table 2 The quantum yields of the conversion of 2MeONp and product **3**

[AA]/mmol dm^3	Conversion of 2MeONp %	Conversion of 2MeONp Φ_c	Φ_c°/Φ_c	Yield of 3 %	Yield of 3 Φ
Trifluoroacetic acid in acetonitrile[a]					
0	32.4	—	1.0	32.4	—
1	25.4	—	1.3	19.0	—
2	23.5	—	1.4	17.2	—
3	21.9	—	1.5	14.8	—
4	20.8	—	1.6	13.2	—
8	16.5	—	2.0	10.2	—
10	14.2	—	2.3	8.9	—
H_2SO_4 in methanol[b]					
0	14.1	0.020	1.0	7.4	0.011
0.1	12.8	0.019	1.1	6.0	0.009
0.5	11.6	0.017	1.2	5.4	0.008
1.0	10.4	0.014	1.4	4.2	0.006
10.0	7.8	0.012	1.7	2.7	0.004
H_2SO_4 in acetonitrile[b]					
0.0	12.8[c] (38.0)	0.029	1.0	2.0[c] (30)	0.021
0.1	11.6[c] (34.3)	0.026	1.1	10.1[c] (28) 0.015	0.015
0.5	26.9	0.019	1.5	15.9	0.012
1.0	24.0	0.017	1.7	11.4	0.006
10.0	19.0	0.014	2.1	4.7	0.003

[a] The quantum yields were not determined. [2MeONp] = 0.01 mol dm^{-3}, [AA] = 0.05 mol dm^{-3}. [b] [MeONp] = 0.01 mol dm^{-3} and [AA] = 0.1 mol dm^{-3}; the quantum yields were determined by means of benzophenone–benzohydrol actinometry; other conditions were the same as for the CF_3COOH experiment. [c] The irradiation time for these two experiments was 10 min, and the extrapolated percentages for 30 min are given in brackets.

These photocycloaddition products were established from their spectral data that proved their functional groups and relative orientations. The critical evidence for regioisomers **3** and **7** was gained from ^{1}H NMR chemical shifts for the CH_2 group at 3.87 and 4.48 ppm, respectively; the 1-acetonyl group in **7** should manifest itself at a lower field by the deshielding from the neighbouring benzene ring. The ^{1}H NMR spectra of **4a** and **4b** were very similar showing corresponding signals except that **4a** showed an extra CH_3 singlet at 4.13 ppm. As this signal appeared in a substantially more deshielded position than ordinary aromatic methoxy groups (*ca.* 3.7 ppm), we propose the structure **4**. The structure of **5** was assigned with the acetyl group at C-4, which showed the corresponding ring proton signal at 3.78 ppm as a doublet; the *J*-value of 6.5 Hz is closer to a *cis*-configuration in analogous cyclohexadienyl derivatives reported in the literature.[13,17]

The photocycloaddition of 1-naphthol and 2-naphthol to AA under comparable conditions occurred more slowly than the above cases and gave complex product mixtures, probably from secondary reactions. **3** and **7**, among other minor compounds, could be detected in the crude mixture. Since the isolations proved to be difficult, these photoreactions were not probed further.

The mechanism of the photocycloaddition was investigated mainly using 2MeONp as a model because of the simpler product pattern. Owing to absorption overlap as in Fig. 1, the irradiation with the 300 nm light source (RPR 3000 Å) simultaneously excited both MeONp and AA. The decision of which excited species initiates the photocycloaddition was not trivial, and was further complicated by excimer formation (*vide infra*).[14b] These factors and high conversion percentage led to

Table 3 The quantum yields of the conversion of 1MeONp and product **5**

$[H_2SO_4]$/ mmol dm^{-3}	Conversion %	Conversion Φ_c	Φ_c^0/Φ_c	Product **5** %	Product **5** Φ
In acetonitrile					
0	34.3	0.027	1.0	9.1	0.005
0.1	33.0	0.025	1.1	7.0	0.004
0.5	21.6	0.017	1.6	6.2	0.0038
1.0	12.0	0.009	3.0	1.6	0.001
10.0	10.0	0.008	3.4	1.2	0.0008
In methanol					
0.0	26.0	0.020	1.0	8.6	0.004
0.1	23.9	0.018	1.1	5.4	0.0026
0.5	18.6	0.014	1.4	4.3	0.002
1.0	11.0	0.009	2.2	1.4	0.0006
1.5	7	0.005	4.0	—	—

the wrong conclusion that excited AA was initiating the photoreaction in a previous communication.[7] Irradiation with a 350 nm light source (RPR 3500 Å) on 2MeONp (0.5 mol dm^{-3}) and AA (0.01 mol dm^{-3}) gave a good quantum yield of 0.015 in which the incipient energy was primarily absorbed by 2MeONp ($\geqslant$85%). In addition, both the photocycloaddition and fluorescence intensity of 2MeONp were efficiently quenched by oxygen, biacetyl and methyl iodide. Since singlet excited MeONp (E_S = 85–87 kcal mol^{-1} in polar solvents)[16] could not possibly sensitize AA, MeONp should be the reacting species. Singlet state AA, having a short lifetime, could not be the reactive species initiating the photocycloaddition process. This conclusion agrees with that found in a similar photocycloaddition of methyl 2-naphthoate.[13,14] For both cases triplet-state cycloadditions were eliminated by the failure of benzophenone (or xanthone) to sensitize the formation of **3**, **5** and **7**.

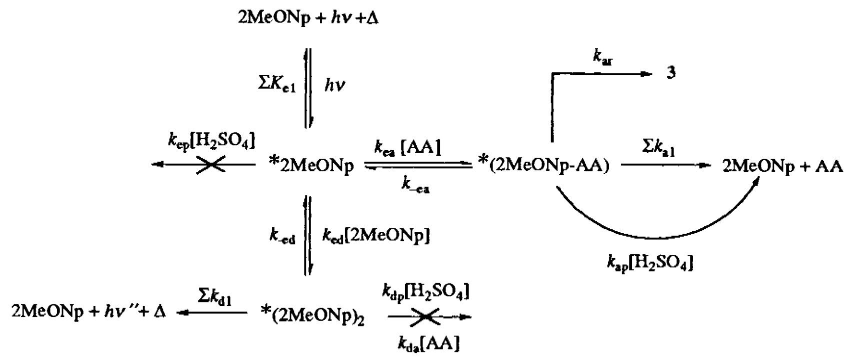
Surprisingly, in the photocycloaddition of MeONp to AA, the quantum yield of MeONp conversions as well as that of the formation of **3** and **5** were reduced in the presence of H_2SO_4 in the millimolar region (Tables 2 and 3). The product formation was reduced much more rapidly than MeONp conversion, Φ_c. Other acids also caused similar effects but to a lesser extent, except for TFA (Table 2). At $[H_2SO_4] < 0.01$ mol dm^{-3} the acid-catalysed aldol condensation was too slow to be noticeable under comparable non-photolytic conditions. In methanol and acetonitrile, whereas **3** was photolytically decomposed by 10% in 1 h in both cases, the percentage was dramatically increased in the presence of 0.01 mol dm^{-3} H_2SO_4 to 45 and 46%, respectively, after irradiation for 30 min. Though the photodecomposition products were not identified, the acid-catalysed secondary photoreaction of **3** and **5** was proved to be facile, and this rendered their quantum yields useless for the analysis of the primary photoprocess. It is clear that the quantum yield of 2MeONp and 1MeONp conversions (Φ_c in Tables 2 and 3) are drastically reduced by TFA and H_2SO_4 even in the sub-millimolar region. Two control experiments were also run to probe the acid effects. Both the photocycloaddition of AA and cyclohexene (a de Mayo reaction) in the presence and absence of trifluoroacetic acid showed the same quantum yield of 1-acetyl-2-acetonylcyclohexane. This eliminated the possibility that the cyclobutyl intermediate (which arises from the [2 + 2] photocycloaddition) could be catalytically decomposed by acid to the starting material. Secondly, the product quantum yields were determined to become lower as the conversion was higher than 10%: thus the previous kinetic analysis obtained by high conversions[7] (to ascertain analytical accuracy) must cause an erroneous conclusion (*vide infra*). Such effects on product quantum yield are analogous (but in the opposite sense) to the case of methyl 2-naphthoate with AA and are caused by competing reaction pathways: a detailed analytical analysis has been shown before.[14]

Spectroscopic studies of MeONp

The first order of business was whether H_2SO_4 interacts with the excited- and ground-state MeONp. UV absorption spectroscopy has shown that the spectra of AA and MeONp in methanol and acetonitrile are not changed noticeably in the presence of $[H_2SO_4] < 0.05$ mol dm^{-3}; in the 0.001 mol dm^{-3} region it is certain that either no new protonated species is formed in the ground state or that the AA *cis*-enol tautomer concentration is unaffected.

Fluorescence spectra of 1MeONp have been well established, by Shizuka's publications,[6] to emit from the intramolecular charge transfer state (^1L_a) to give the 340 nm peak in acetonitrile. 2MeONp showed fluorescence maxima at 346 nm in both acetonitrile and methanol; the lowest singlet excited-state energy level was estimated to be 87 kcal mol^{-1} (at 330 nm). At a low concentration ([2MeNOp] = 10^{-4} mol dm^{-3}) the fluorescence intensity of 2MeONp was efficiently reduced by the addition of AA in these solvents without showing a new fluorescence peak: the apparent quenching efficiency was higher in cyclohexane and methanol than in acetonitrile with K_{sv} of 150, 110 and 55 dm^3 mol^{-1}, respectively; this is also qualitatively the order of the AA *cis*-enol tautomer percentage in these solvents.[18] The 2MeONp singlet excited state (^1L_b) lacks intramolecular charge transfer character as supported by the lack of acid-catalysed deuterium exchange and lack of acid quenching of 2MeONp fluorescence.[6] We confirmed that 2MeONp fluorescence was hardly affected by the addition of H_2SO_4 up to 0.05 mol dm^{-3}; this unequivocally eliminated the fluorescence quenching of *2MeONp by acid as an explanation for the acid retardation. Furthermore, for the acid concentrations employed in this retardation study (< 0.01 mol dm^{-3}), the quenching of *1MeONp fluorescence by H_2SO_4 is negligible, hence the same conclusion is applicable here as well.

Since neither the singlet excited state nor the ground state of 2MeONp interacts with acid (TFA or H_2SO_4) to any appreciable extent, the acid retardation of product formation must occur at an intermediate after *2MeONp is quenched by AA (Scheme 2). However, one more complication was encountered: 2MeONp in acetonitrile exhibited reduced fluorescence intensities and gave a new emission peak at about 400 nm as [2MeONp] increased from 5 × 10^{-3} to 1.0 mol dm^{-3} (Fig. 2). At the increasing concentrations in this range, internal filter effects due to 2MeONp absorption in the 320–350 nm region artificially shaved the fluorescence spectra from the low wavelength side: the peaks are artifacts.[14b] Using a front-face arrangement for fluorescence, a similar spectral pattern was observed, obviously arising from an emission–reabsorption sequence. The new fluorescence band at *ca.* 400 nm could not be attributed to this mechanism, and was obviously arising from the excimer emission. The excimer emission started to show at [2MeONp] > 0.01 mol dm^{-3} where most photocycloaddition was carried out. At [2MeONp] = 0.15 mol dm^{-3}, H_2SO_4 up to 0.01 mol dm^{-3} did not affect the intensity of either *2MeONp or its excimer fluorescence peaks (Fig. 3). Also, AA concentrations up to 0.05 mol dm^{-3} quenched both *2MeONp and its excimer (monitored at 370 and 450 nm for *2MeONp and its excimer, respectively) at an equal proportion, which indicates that the excimer was not interacting with AA.[14b] Though the 2MeONp excimer is a non-reactive transient (Scheme 2), its formation and decay do pose complications in the process dynamics as we encountered in a previous case.[14b,c]



Scheme 2

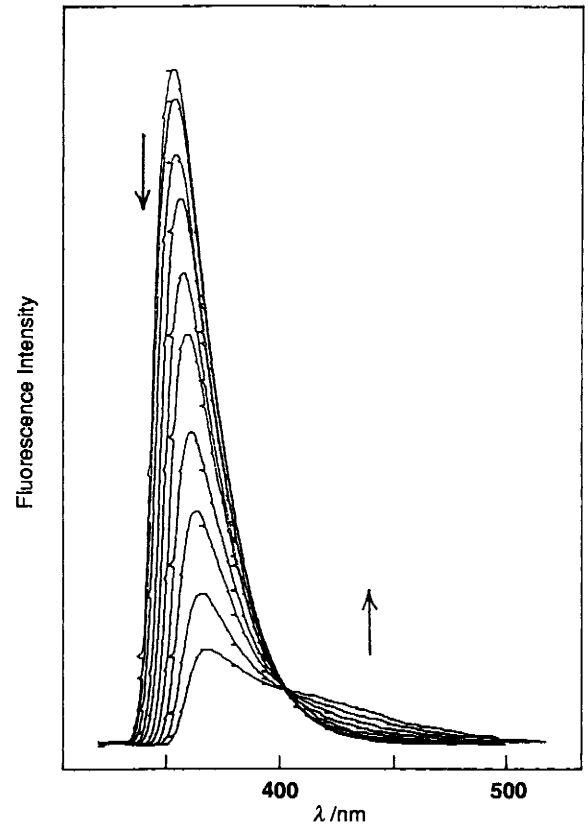


Fig. 2 The fluorescence spectra of 2MeONp in acetonitrile at concentrations 0.0048, 0.0096, 0.0192, 0.0384, 0.077, 0.154, 0.31, 0.62, 1.24 and 2.48 mol dm^{-3} and λ_{ex} = 327 nm; note the internal filter effect at 330–350 nm

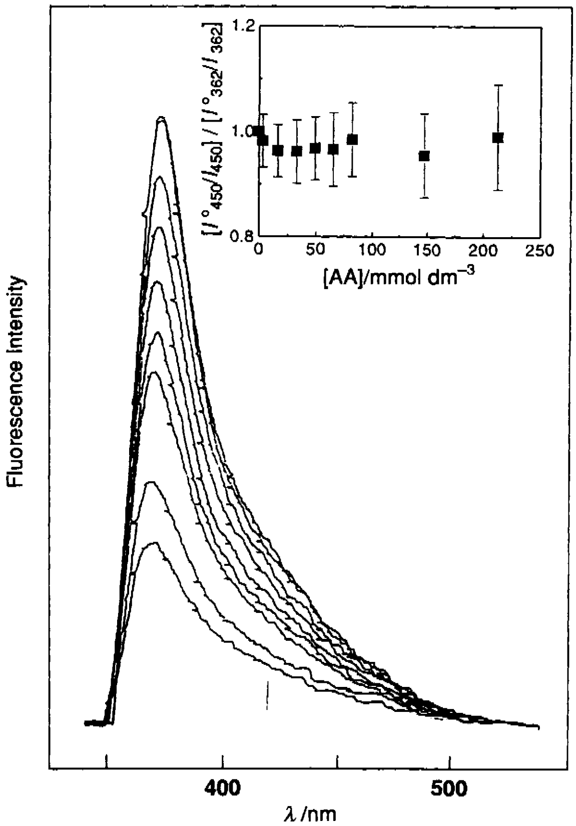


Fig. 3 Quenching of the fluorescence intensities of 2MeONp (0.62 mol dm^{-3}) in acetonitrile by AA (0–0.21 mol dm^{-3}); λ_{ex} = 327 nm using front face orientation. The plot of $[I^{o}_{450}/I_{450}]/[I^{o}_{362}/I_{362}]$ *vs.* [AA] is a horizontal straight line up to 0.21 mol dm^{-3}.

Exciplex quenching by H_2SO_4

In Scheme 2, the reaction pattern of singlet excited 2MeONp is summarized with the appropriate kinetic parameters according to the results up to this point. The quenching of the exciplex (2MeONp–AA) by acid is assumed in analogy to that observed in the methyl 2-naphthoate–AA photocycloaddition.[14] We shall apply EFQ[15] analysis to establish a similar interaction and relate it to the acid retardation. At low concentrations used for the fluorescence studies, the excimer process is negligible: k_{dp}, k_{da} and k_{ep} are insignificant as shown above. The unimolecular decays of each transient are Σk_{e1}, Σk_{a1} and Σk_{d1} that also include fluorescence rate constant k_{ef}, k_{af} ($\cong 0$) and k_{df} and also k_{ar}. The first step was to establish the physical existence of the exciplex and its reversibility (*i.e.*, the relative size of k_{-ea} to Σk_{a1}). Eqn. (1) was derived previously[14c,19] to represent the fluorescence quenching by AA under oxygen where $k_{ox}[O_2]$, the rate of quenching by oxygen, is the same for any excited species in the same solvent on the basis of diffusion-controlled encounter frequency.

$$I^{o}_{e}/I_{e} = 1 + K^{o}_{SV}[O_2] + K^{a}_{SV}[AA] \qquad (1a)$$

where $K^{a}_{SV} = k_{ea}\alpha\tau^{o}_{e}$, $K^{o}_{SV} = k_{ox}\tau^{o}_{e}$ and

$$\alpha = (\Sigma k_{a1} + k_{ox}[O_2])/(k_{ea} + k_{ox}[O_2] + \Sigma k_{a1}) \qquad (1b)$$

$$\alpha^{o} = \Sigma k_{a1}/(k_{-ea} + \Sigma k_{a1}) \quad \text{under Argon} \qquad (1c)$$

I^{o}_{e} and I_{e} are the *2MeONp fluorescence intensities in the absence and presence of both AA and oxygen, α is the efficiency factor with which the exciplex decays to the ground state, and τ^{o}_{e} is the *2MeONp fluorescence decay lifetime

Table 4 Quenching of 2MeONp fluorescence by AA in the presence and absence of oxygen

Conditions	$[O_2]$/mmol dm^{-3} [a]	$K^{o}_{SV}[O_2]$	$k_{ox}[O_2]/10^{-7}$ s^{-1}	K^{a}_{SV}/dm^3 mol^{-1}	$k_{ea}\alpha/10^9$ dm^3 mol^{-1} s^{-1}
In acetonitrile					
Argon	0	0	0	55 ± 3	3.8 ± 0.2
Air	1.9	0.78 ± 0.04	5.4 ± 0.3	68 ± 3	4.7 ± 0.2
O_2	9.1	3.72 ± 0.19	25.8 ± 1.3	106 ± 5	7.4 ± 0.4
In methanol					
Argon	0	0	0	109 ± 5	8.0 ± 0.4
Air	2.1	0.78 ± 0.04	5.7 ± 0.3	121 ± 6	8.9 ± 0.4
O_2	10.2	3.70 ± 0.19	27.2 ± 1.4	157 ± 8	11.5 ± 0.6

[a] Ref. 16.

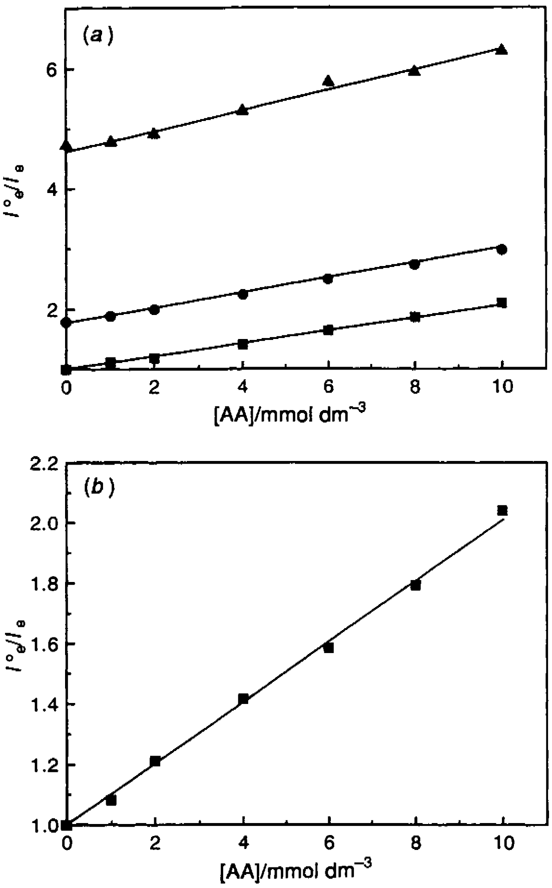


Fig. 4 (*a*) Plots of (I^{o}_{e}/I_e) *vs.* [AA] under argon (■), air (●) and pure oxygen (▲); (*b*) a typical plot of (I^{o}_{e}/I_e) *vs.* [AA] in the presence of a fixed concentration of H_2SO_4 (10.8 mmol dm^{-3}) in acetonitrile under argon

under argon at a concentration less than 10^{-4} mol dm^{-3} (negligible excimer formation). From these plots [Fig. 4(*a*)], the intercept gives $1 + K^{o}_{SV}[O_2]$ and the slope K^{a}_{SV}. The lifetimes of *2MeONp are derived from $K^{o}_{SV}/k_{ox} = \tau^{o}_{e}$, and the apparent quenching rate constant is $k_{ea}\alpha = K^{a}_{SV}/\tau^{o}_{e}$. It was noted that $k_{ea}\alpha$ increases with increasing $k_{ox}[O_2]$ term; this indicates that k_{-ea} is significant with respect to the magnitude of Σk_{a1} and $k_{ox}[O_2]$. These results are listed in Table 4.

Having established the presence of k_{-ea}, the next step was to use H_2SO_4, instead of oxygen, as the perturber to examine the protonation of the exciplex by eqn. (2) according to Scheme 2. Eqn. (2) was derived,[14c,19a,c] in which protonation was represented by the association with H_2SO_4 since in acetonitrile and methanol it is not dissociated.

Table 5 Quenching of 2MeONp fluorescence by AA in the presence of a fixed concentration of H_2SO_4

$[H_2SO_4]$/mmol dm^{-3}	K^{h}_{SV}/dm^3 mol^{-1}	$k_{ea}\beta/10^9$ dm^3 mol^{-1} s^{-1}
In acetonitrile τ^{o}_{e} = 14.4 ns		
0	55 ± 3	3.8 ± 0.2
3.6	58 ± 3	4.0 ± 0.2
10.8	64 ± 3	4.4 ± 0.2
In methanol τ^{o}_{e} = 13.6 ns		
0	109 ± 5	8.0 ± 0.4
1.1	111 ± 6	8.2 ± 0.4
10.8	120 ± 6	8.8 ± 0.4

$$I^{o}_{e}/I_e = 1 + k_{ep}\tau^{o}_{e}[H_2SO_4] + k^{h}_{SV}[AA] \qquad (2a)$$

$$\text{where } k_{ep} = 0,\ K^{h}_{SV} = k_{ea}\beta\tau^{o}_{e} \qquad (2b)$$

$$\beta = (\Sigma k_{a1} + k_{ap}[H_2SO_4])/(k_{-ea} + k_{ap}[H_2SO_4] + \Sigma k_{a1}) \qquad (2c)$$

I^{o}_{e} and I_e are the intensity of *2MeONp fluorescence in the absence and presence of both H_2SO_4 and AA. The plots [Fig. 4(*b*)] at fixed $[H_2SO_4]$ concentrations in acetonitrile converged on unity at [AA] = 0 (since $k_{ep} = 0$) with different slopes ($= K^{h}_{SV}$) as listed in Table 5. K^{h}_{SV} showed small increase with $[H_2SO_4]$ indicating the presence of the $k_{ap}[H_2SO_4]$ term.

Discussion

The approach of AA to singlet excited 2MeONp must have a transition state leading to the orientation shown in **1** that eventually leads to **2**; for the reaction with *1MeONp, the orientation must be reversed regardless of the attack at the C-1,2 or C-3,4 position to give **7** and **5**.

It is known that H_2SO_4 does not dissociate to a large extent in acetonitrile and methanol.[20] It is also known that for AA the *cis*-enol tautomer percentage increases at higher concentrations,[18] but in the [AA] ⩽ 0.05 mol dm^{-3} region, where most fluorescence quenching and product quantum yield experiments were carried out, the increase is calculated to be less than 1%. Because of this the total AA concentration has been used for calculation without correction for the actual *cis*-enol tautomer concentration.

Having eliminated the interaction of acid with both ground- and excited-state MeONp, the intermediate responsible for the observed acid retardation must be a downstream derivative. Fortunately, the excimer does not react with H_2SO_4 and AA, and its formation process can also be excluded. The possibility that the cyclobutyl derivative **1** is the acid-sensitive species is less likely for various reasons. First, acid catalysis at

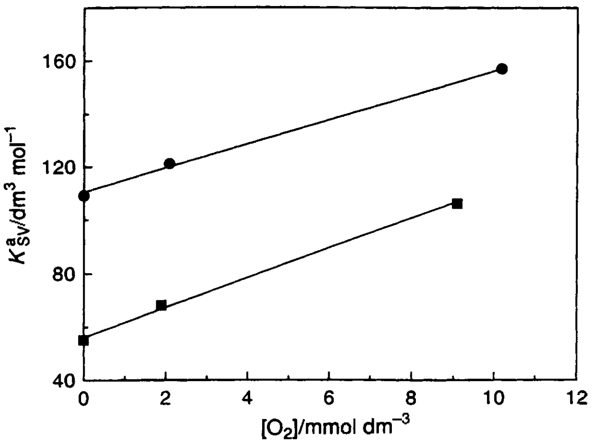


Fig. 5 Plot of K^a_{SV} *vs.* $[O_2]$ in acetonitrile (■) and methanol (●)

$[H_2SO_4] < 0.001$ mol dm^{-3} for a two-bond breaking process in the ground state **1** is not likely to be efficient. Second, the lack of acid effects in the photocycloaddition of AA and cyclohexene (the de Mayo Reaction) indirectly indicates that such analogous cyclobutane compounds are not likely to be responsive to acid effects. In analogy to the acid catalysis in the photocycloaddition of methyl 2-naphthoate, the exciplex from *2MeONp and AA is most likely the key intermediate and sensitive to acid effects.

As *(2MeONp–AA) is non-fluorescent, the EFQ method[15] was applied to probe the interaction of this transparent exciplex with H_2SO_4. In view of the extensive kinetic analysis required for a complicated quenching pattern as experienced in the naphthoate case,[14] the present effort is limited to establish the presence of an acid interaction with the *(2MeONp–AA) exciplex semiquantitatively. By design, the interaction of *2MeONp with H_2SO_4 is negligible,[6] that is, k_{ep} is negligible, which facilitates analysis. While the excimer formation becomes significant at $[2\text{MeONp}] > 0.01$ mol dm^{-3}, the excimer is a non-reactive intermediate contributing nothing but to bleed *2MeONp into an energy-wasting short circuit. It should be pointed out that this process causes a low quantum yield of the photocycloaddition at high 2MeONp concentrations. Therefore progressively higher quantum yields occur at higher conversions. This is the source of the erroneous conclusion in the communication[7] (*vide supra*).

Fig. 5 shows a reasonable linear plot of K^a_{SV} against $[O_2]$ from the data in acetonitrile and methanol (Table 4) with slopes (intercepts) of 5540 dm^3 mol^{-1} (56 dm^3 mol^{-1}) and 4520 dm^3 mol^{-1} (110 dm^3 mol^{-1}), respectively. These linear plots indicate the presence of a non-fluorescent successor species of the *(2MeONp–AA) exciplex. In addition, a linear relationship occurs only under the condition that $k_{ox}[O_2] \approx \Sigma k_{a1} \ll k_{-ea}$ in eqn. (1). It should be noted that the provision $k_{ox}[O_2] \approx \Sigma k_{a1}$ is required to observe a positive slope in Fig. 5, *i.e.*, if $\Sigma k_{a1} \gg k_{ox}[O_2]$, otherwise one would expect to observe a near horizontal line.

$$K^a_{SV} = K_{ea}\tau^\circ_e(\Sigma k_{a1} + k_{ox}[O_2]) \quad \text{where } K_{ea} = k_{ea}/k_{-ea} \qquad (3)$$

It follows that $\Sigma k_{a1}/k_{ox}$ = (intercept)/(slope); if k_{ox} is assumed to be equal to k_{diff} for oxygen-quenched systems (2.9×10^{10} dm^3 mol^{-1} s^{-1} and 1.8×10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile and methanol,[16] respectively), Σk_{a1} is calculated to be 2.9×10^8 s^{-1} and 4.3×10^8 s^{-1} in acetonitrile and methanol, respectively. As the slope = $K_{ea}\tau^\circ_e\, k_{ox}$ and as both k_{ox} and τ°_e are known, K_{ea} can be calculated; K_{ea} = 13.2 dm^3 mol^{-1} and 18.6 dm^3 mol^{-1} in acetonitrile and methanol, respectively. On the basis that $k_{-ea} \gg \Sigma k_{a1}$ and that K_{ea} is greater than one, the magnitude of Σk_{a1} suggests that k_{-ea} is of the order of 10^9 s^{-1} and that k_{ea} is of the order of 10^{10} dm^3 mol^{-1} s^{-1}. Adapating $k_{ea} = k_{diff}$, k_{-ea} can be estimated to be 2.2 and 1.0×10^9 s^{-1}. These parameters are summarized in Table 6.

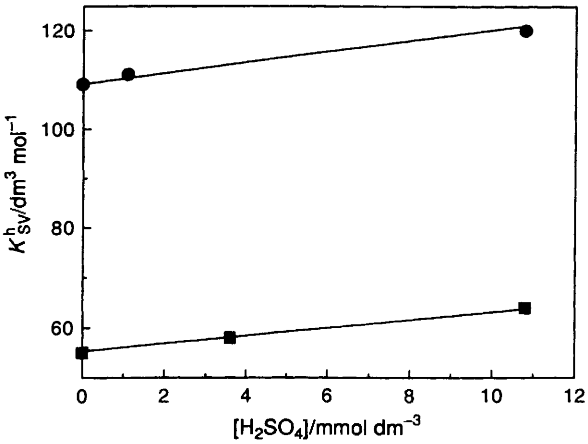


Fig. 6 Plot K^h_{SV} *vs.* $[H_2SO_4]$ in acetonitrile (■) and methanol (●)

Table 6 Estimated rate constants

	Acetonitrile	Methanol
K_{ea}/dm^3 mol^{-1}	13.2 ± 0.9	18.6 ± 1.3
$k_{ea} = k_{diff}/10^{10}$ dm^3 mol^{-1} s^{-1} [a]	2.9 ± 0.5	1.8 ± 0.3
$k_{-ea}/10^9$ s^{-1}	2.2 ± 0.4	1.0 ± 0.2
$\Sigma k_{a1}/10^8$ s^{-1}	2.9 ± 0.3	4.3 ± 0.4
$k_{ap}/10^9$ dm^3 mol^{-1} s^{-1}	4.3 ± 0.4	6.5 ± 0.7

[a] Ref. 16.

Having established that the *(2MeONp–AA) exciplex exists, its interaction with acid must be demonstrated to verify that the acid retardation indeed occurs at this step. Repeating the EFQ analysis, using H_2SO_4 in place of O_2, the obtained K^h_{SV} values in acetonitrile and methanol (Table 5) are plotted against $[H_2SO_4]$ (Fig. 6). The linear plots in Fig. 6, similar to the perturbation by oxygen (Fig. 5), suggests that $k_{ap}[H_2SO_4] \approx \Sigma k_{a1} \ll k_{-ea}$; *i.e.*, the *(2MeONp–AA) exciplex is quenchd by acid. The values of k_{ap} can be calculated from the ratio of the slopes in Fig. 5 (S_5) divided by the slopes in Fig. 4 (S_4).

$$S_5/S_4 = k_{ap}/k_{ox} = k_{ap}/k_{diff} \qquad (4)$$

Values of S_5/S_4 were calculated to be 0.145 and 0.361 in acetonitrile and methanol, respectively; k_{ap} is estimated to be 4.3×10^9 dm^3 mol^{-1} s^{-1} in acetonitrile and 6.5×10^9 dm^3 mol^{-1} s^{-1} in methanol. These values show that the interaction between *(2MeONp–AA) with H_2SO_4 is efficient. The larger k_{ap} value in methanol probably reflects that H_2SO_4 is a stronger acid in methanol than in acetonitrile.[20] In comparison with the acid quenching of the *(methyl 2-naphthoate–AA) exciplex by H_2SO_4, the same trend for k_{ap} between acetonitrile and methanol is observed and the k_{ap} values are about twice as large; *e.g.*, the *(2MeONp–AA) exciplex is quenched faster by H_2SO_4 than the *(methyl 2-naphthoate–AA) exciplex.

The EFQ analysis above shows that the interaction of the *(2MeONp–AA) exciplex with H_2SO_4 is indeed efficient. It is concluded that acid retardation of **3** established by the product quantum yield studies, must arise from the catalysed demotion of the quenching of the *(2MeONp–AA) exciplex to the ground state by acid. Therefore, Scheme 2 depicts a realistic interpretation of the acid retardation of the photocycloaddition of singlet excited MeONp with AA.

Experimental

General

Spectroscopic and GC analytical apparatus as well as their operating conditions were the same as those published in a similar study.[13,17] Commercial products of 1MeONp and 2MeONp were from Aldrich; the former was distilled at 132–135 °C (10 mmHg), and the latter was recrystallized from light petroleum to give mp 70–73 °C. Acetylacetone (BDH) was distilled.

Photocycloaddition of 1MeONp with AA

A solution of 1MeONp (300 mg) and AA (500 mg) in CH$_3$CN (50 cm^3) was distributed in 8 quartz tubes and purged with N$_2$. These tubes were irradiated in a Rayonet Reactor with RPR 3000 Å lamps for 12 h. GC analysis of the photolysate showed 64% conversion and new products at t_R = 7.48 min (33%) and 7.67 min (8%) and other peaks. Flash chromatography (20% ethyl acetate in hexanes) of the crude product afforded fractions containing *cis*-1-methoxy-3-acetonyl-4-acetyl-3,4-dihydronaphthalene (**5**, 73 mg) and a small amount of 1-acetonyl-2-acetylnaphthalene (**7**). Some of latter fractions contained mainly **6** as shown by GC–MS and GC–FT-IR: *m/z* 258 (M$^+$, 10%), 215 (50), 200 (80), 158 (100), 115 (35) and 43 (20); ν_{max}/cm^{-1} 1730s, 1572m, 1470m, 1445m, 1360m, 1266s, 1161m, 1090w and 804m. This fraction (20 mg) was adsorbed onto silica gel and eluted to give **7** (17 mg) which was distilled: *m/z* 226 (M$^+$, 30%), 211 (25), 184 (31), 169 (100), 141 (35), 115 (12) and 43 (8); ν_{max}/cm^{-1} 1730m, 1703s, 1666w, 1360m, 1234m, 1150w, 1123w, 808m and 743w; δ(CDCl$_3$) 2.30 (s, 3 H), 2.70 (s, 3 H), 4.48 (s, 2 H), 7.6 (m, 2 H), *ca.* 7.9 (m, 3 H) and 8.0 (m, 1 H). The earlier fractions were rechromatographed to give **5** (73 mg) as an oil: δ_H(CDCl$_3$) 2.01 (s, 3 H), 2.18 (s, 3 H), 2.57 (dd, J = 18.0 and 8.0 Hz, 1 H), 2.87 (dd, J = 18.0 and 8.0 Hz), 3.5 (m, 1 H), 3.65 (s, 3 H), 3.78 (d, J = 6.5 Hz, 1 H), 4.72 (d, J = 3.0 Hz, 1 H), 7.4 (m, 3 H) and 7.56 (m, 1 H); ν_{max}/cm^{-1} 1730s, 1643m, 1362s, 1232m, 1159m, 1101m and 768w; *m/z* (EI) 258 (M$^+$, 10%), 215 (80), 200 (100), 185 (50), 173 (45), 158 (90), 141 (30), 128 (30), 115 (39) and 43 (35); δ_C(CDCl$_3$) 207.4, 207.2, 151.1, 133.2, 131.0, 129.6, 128.3, 127.9, 122.5, 97.3, 57.0, 54.7, 47.8, 40.4, 29.7 and 28.4 (Found: C, 74.7; H, 7.0. Calc. for $C_{16}H_{18}O_3$: C, 74.78; H, 7.01%).

Photocycloaddition of 2MeONp with AA

A solution of 2MeONp (300 mg) and AA (500 mg) in acetonitrile was irradiated under the same conditions as above for 9 h to afford a single product (73%) which was flash chromatographed to give colourless crystals (150 mg). Recrystallization from EtOAc–hexane gave 1-acetyl-2-acetonylnaphthalene **3**, mp 67–69 °C; δ_H(CDCl$_3$) 2.23 (s, 3 H), 2.66 (s, 3 H), 3.87 (s, 2 H), 7.28 (d, J = 8 Hz, 1 H), 7.5 (m, 2 H), 7.68 (d, J = 8 Hz, 1 H) and 7.9 (m, 2 H); δ_C(CDCl$_3$) 207.5, 205.3, 139.7, 132.5, 129.45, 129.1, 128.5, 128.1, 127.3, 127.1, 126.2, 124.4, 48.1, 33.1 and 29.1; ν_{max}/cm^{-1} 1713s, 1508m, 1427w, 1360m, 1204 (1159), 957w, 822w and 746w; *m/z* (EI) 226 (M$^+$, 20%), 225 (10), 211 (13), 184 (17), 169 (66), 153 (100), 141 (24), 123 (16) and 43 (13); λ_{max}(CH$_3$OH)/nm 292 (ε = 4400 dm^3 mol^{-1} cm^{-1}), 280 (5240) and 271sh (4700) (Found: C, 79.8; H, 6.25. Calc. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%).

Cyclization of 3

Compound **3** (100 mg) and 10 drops of concentrated HCl in acetonitrile (15 cm^3) were refluxed for 10 min to show GC peaks at 4.46 and 5.47 min in a 2:1 ratio. Preparative TLC of the crude product gave 1-methoxy-3-methylphenanthrene (**4a**) and 1-hydroxy-3-methylphenanthrene (**4b**). The major product **4a** was recrystallized from cyclohexane to give light yellow crystals; mp 73–74 °C, *m/z* 222 (M$^+$, 100%), 207 (42), 179 (45), 178 (50), 89 (18) and 76 (12); δ_H(CDCl$_3$) 2.57 (s, 2 H), 4.13 (s, 3 H), 6.99 (d, J = 1.5 Hz, 1 H), 7.33 (s, 1 H), 7.57 (dt, J = 8.0 and 1.0 Hz, 1 H), 7.63 (ddd, J = 8.0, 8.5 and 2.0 Hz, 1 H), 7.65 (d, J = 9.0 Hz, 1 H), 7.72 (d, J = 9.0 Hz, 1 H), 7.88 (dd, J = 8.0 and 1.5 Hz, 1 H) and 9.62 (d, J = 8.5 Hz, 1 H); ν_{max}/cm^{-1} IR 3057s, 2930s, 1622s, 1456s, 1402m, 1306m, 1217m, 1142s, 1084s and 744s; δ_C(CDCl$_3$) 158.8, 136.5, 134.8, 132.5, 130.5, 128.3, 128.2, 128.0, 126.9, 126.3, 125.4, 121.4, 118.8, 110.2, 55.7 and 21.6.

Compound **4b** was recrystallized from ethanol–benzene to afford light brown crystals: mp 111–113 °C, δ_H(CDCl$_3$) 2.50 (s, 3 H), 2.50 (s, 3 H), 5.62 (s, 1 H), 6.81 (s, 1 H), 7.31 (s, 1 H), 7.56 (ddd, J = 7.5, 7.5 and 1.0 Hz, 1 H), 7.63 (ddd, J = 8.5, 7.5 and 1.5 Hz, 1 H), 7.62 (d, H = 9.0 Hz, 1 H), 7.86 (dd, J = 7.5 and 1.5 Hz, 1 H) and 9.85 (dd, J = 8.5 and 1.0 Hz, 1 H); δ_C(CDCl$_3$) 154.2, 136.5, 135.2, 132.4, 130.4, 128.3, 128.2, 128.1, 126.8, 126.5, 125.6, 121.7, 114.9, 117.8 and 21.1; ν_{max}/cm^{-1} 3641s, 3055s, 2932m, 1628s, 1410m, 1227s, 1177m, 1128m, 829m and 744s; *m/z* 208 (M$^+$, 100%), 179 (30), 165 (32), 89 (13), 76 (11) and 63 (3).

Triplet sensitization

Acetonitrile solution (5 cm^3) containing 2MeONp (0.005 mol dm^{-3}), AA (0.10 mol dm^{-3}) and octadecane (0.005 mol dm^{-3}) were placed in three tubes. The first tube contained xanthone (0.05 mol dm^{-3}, E_T = 71 kcal mol^{-1}), the second benzophenone (0.05 mol dm^{-3}, E_T = 69 kcal mol^{-1}) and the third was the control. These tubes were purged with nitrogen and irradiated with RPR 3500 Å lamps (at 350 nm) for 60 min. GC analysis showed the disappearance of 2MeONp (40%) and the formation of **3** (35%) for the control solution but that of the other two showed no change of the reactants except a small decrease in sensitizers. The photolysis was repeated with 2MeONp (0.1 mol dm^{-3}), AA (0.1 mol dm^{-3}) and sensitizers (0.05 mol dm^{-3}) to give similar results. Similar experiments were also carried out with 1MeONp giving similar results.

Quantum yield determinations

Solutions (5 cm^3) containing predetermined concentrations of 2MeONp, AA and octadecane (internal standard, 0.005 mol dm^{-3}) were each placed in quartz tubes. These solutions were sealed and purged with nitrogen. The tubes were irradiated in a merry-go-round with RPR 3500 Å lamps (16 × 24 W) for 10–40 min to cause 10–14% conversions of 2MeONp. The products were analysed by GC and the yields were calculated against the internal standard. Quantum yields were calculated with respect to benzhydrol (0.2 mol dm^{-3})–benzophenone (0.1 mol dm^{-3}) actinometry (Φ = 0.74).[16]

The cycloaddition of AA with cyclohexene

A hexane solution of acetylacetone (0.05 mol dm^{-3}) and cyclohexene (0.5 mol dm^{-3}) was distributed in quartz tubes: three of them contained trifluoroacetic acid (0.005 mol dm^{-3}) and the other three served as reference. These were purged with argon and irradiated with RPR 3000 Å lamps for 4 h. GC analysis showed that the yields of 1-acetonyl-1-acetylcyclohexane were 13.4, 12.6 and 14.0% for the first three tubes, and 14.4, 13.8 and 12.9% for the last three tubes.

Effects of acid

Acetonitrile solutions containing 2MeONp (0.01 mol dm^{-3}), AA (0.05 mol dm^{-3}) in acetonitrile and TFA ranging 0.001–0.01 mol dm^{-3} were sealed under nitrogen in quartz tubes; these were irradiated with 300 nm lamps (RPR 3000 Å) in a merry-go-round for 30 min. The photolysates were mixed with a naphthanlene standard solution (0.01 mol dm^{-3}) and analysed with GC (HP-1 capillary column, 150–230 °C at 10 °C min^{-1}) as shown in Table 2. The effects of H$_2$SO$_4$ were also determined in a similar way and are listed in Table 2. The quantum yields of conversion of 1MeONp and of the product **5** were also determined in the presence and absence of H$_2$SO$_4$ using

[2MeONp] = 0.01 mol dm^{-3} [AA] = 0.1 mol dm ^{3}, and 300 nm irradiation for 1 h. The results are summarized in Table 3.

References

1 J. J. McCullough, *Chem. Rev.*, 1987, **87**, 811.

2 P. A. Wendel and T. W. von Geldern in *Photochemistry in Organic Synthesis*, ed. J. D. Coyle, Royal Society of Chemistry, London, UK, 1986, ch. 12.

3 B. K. Seliger and M. J. Sterus, *J. Chem. Soc., Chem. Commun.*, 1969, 978.

4 (*a*) T. Teitel, D. Wells, T. H. Spurling and W. H. F. Sasse, *Aust. J. Chem.*, 1978, **31**, 85; (*b*) T. Teitel, D. Wells and W. J. F. Sasse, *Aust. J. Chem.*, 1976, **29**, 1783; (*c*) C. Kowala, G. Sugowdz, W. J. F. Sasse and J. A. Wunderlich, *Tetrahedron Lett.*, 1972, 4721.

5 R. M. Bowman, C. Calvo, J. J. McCullough, R. C. Miller and I. Singh, *Can. J. Chem.*, 1973, **51**, 1060; I. A. Akhtar and J. J. McCullough, *J. Org. Chem.*, 1981, **46**, 1447.

6 (*a*) H. Shizuka, *Acc. Chem. Res.*, 1985, **18**, 141, and papers cited therein: (*b*) H. Shizuka and S. Tobita, *J. Am. Chem. Soc.*, 1982, **104**, 6919.

7 Y. L. Chow, G. E. Buno-Core, X. Y. Liu, K. Itoh and P. Qian, *J. Chem. Soc., Chem. Commun.*, 1987, 913.

8 P. de Mayo, *Acc. Chem. Res.*, 1971, **4**, 41.

9 P. E. Eaton, *Acc. Chem. Res.*, 1968, **1**, 50.

10 A. C. Weedon in *Synthetic Organic Photochemistry*, ed. W. M. Horspool, Plenum, New York, 1984, pp. 61–143.

11 W. Oppolzer, *Acc. Chem. Res.*, 1982, **15**, 135.

12 N. J. Turro, *Modern Molecular Photochemistry*, Benjamin–Cummings, Menlo Park, 1978, ch. 9.

13 (*a*) Y. L. Chow and X. Y. Liu, *Can. J. Chem.*, 1991, **69**, 1261; (*b*) X. Y. Liu, Ph.D. Thesis, Simon Fraser University, 1990.

14 (*a*) Y. L. Chow and C. I. Johansson, *J. Photochem. Photobiol. A: Chem.*, 1993, **74**, 171; (*b*) Y. L. Chow and C. I. Johansson, *Res. Chem. Intermed.*, 1993, **19**, 191; (*c*) Y. L. Chow and C. I. Johansson, *Can. J. Chem.*, 1994, **74**, 2011.

15 Y. L. Chow and C. I. Johansson, *J. Chin. Chem. Soc.*, 1993, **40**, 531.

16 S. L. Murov, G. L. Hug and I. Carmichael, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993, 2nd edn.

17 Y. L. Chow, G. E. Buono-Core, Y. H. Zhang and X. Y. Liu, *J. Chem. Soc., Perkin Trans. 2*, 1991, 2041.

18 (*a*) J. Emsley and N. J. Freeman, *J. Mol. Struct.*, 1987, **161**, 193; (*b*) S. G. Mills and P. Beak, *J. Org. Chem.*, 1985, **50**, 1216.

19 (*a*) J. L. Charlton, D. E. Townsend, B. D. Watson, P. Shannon, J. Kowalewska and J. Saltiel, *J. Am. Chem. Soc.*, 1977, **99**, 5992; (*b*) W. K. Smothers and J. Saltiel, *J. Am. Chem. Soc.*, 1983, **105**, 545; (*c*) T. Majima, C. Pac and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1881.

20 (*a*) O. Popovich and R. P. T. Tomkins, *Nonaqueous Solution Chemistry*, Wiley, New York, 1981, p. 82; (*b*) I. M. Kolthoff and M. K. Chantooni Jr. in *Treatise on Analytical Chemistry, Part 1, 2nd edition*, ed. I. M. Kolthoff and P. J. Elving, Wiley, New York, 1979, pp. 246–247.

Paper 4/07627C
Received 9*th December* 1994
Accepted 10*th March* 1995