The Photocycloaddition of Acetylacetone with Naphthols and their Methyl Ethers

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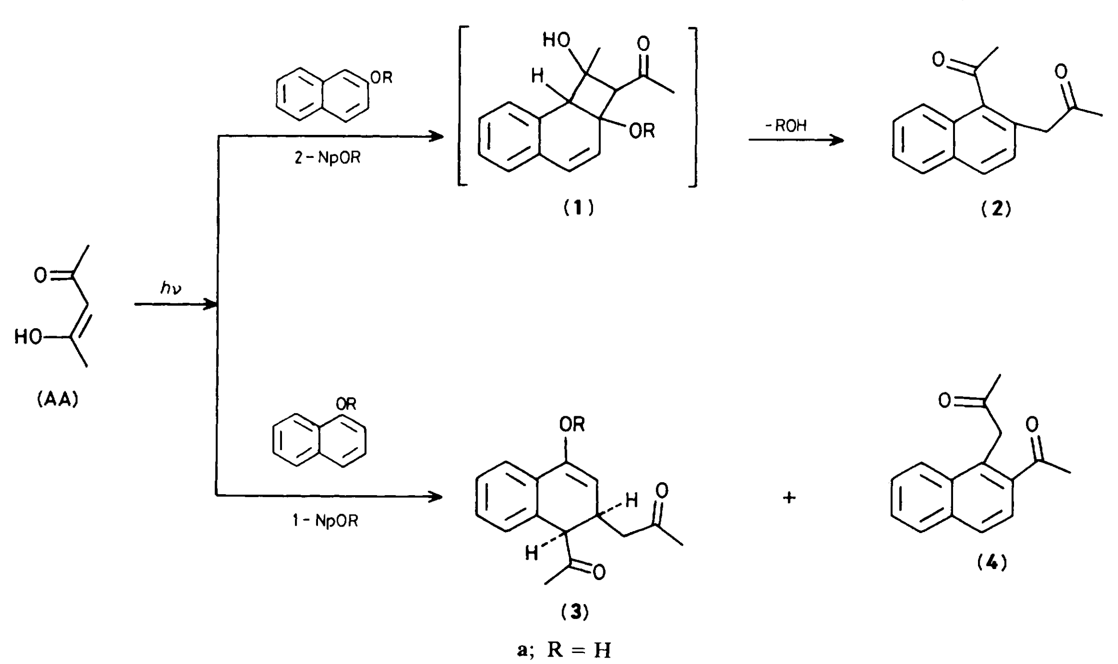
Whereas irradiation of a mixture of a naphthol (or its methyl ether) and acetylacetone with excitation of the naphthol component leads to no reaction, irradiation of a similar mixture with excitation of the acetylacetone component leads to its cycloaddition to the naphthalene derivative to give a cyclobutane as the primary photoproduct.

Among photocycloadditions,[1—4] those involving aromatic compounds carrying CN and CO_2R group attract considerable interest since they provide unique emission properties for theoretical and experimental studies of mechanisms.[5—8] However, there are only few reported examples of photocycloaddition to naphthol derivatives.[9,10] The [2 + 2] photocycloaddition of β-diketones (from their enol forms)[3,4] with alkenes has been widely investigated in synthetic applications.[11] The [2 + 2] photocycloaddition of naphthol derivatives (NpOR) with acetylacetone (AA), while giving useful synthetic intermediates, is strange in that commonly recognized excited states of reactants are not likely to be involved.

Shown in the Scheme 1 is the pattern of the photoaddition in acetonitrile (or in other solvents) of AA (enol form) to 2-naphthol (2-NpOH) and 1-naphthol (1-NpOH) and their corresponding methyl ethers (2-NpOMe and 1-NpOMe) to give (**2**) and (**3**) + (**4**) as the products respectively. The [2 + 2] photocycloadducts [*e.g.* (**1**)] were assumed to be the primary products, and indeed (**1**) (or its isomers) was detected by gas chromatography–mass spectrometry. The structures of (**2**)—(**4**) were assigned on the basis of their spectroscopic properties. The orientation of the two side chains in (**2**) and (**4**) was indicated by the lower field CH_2 singlet in (**4**) (δ 4.48) than that of (**2**) (δ 3.87). I.r. and n.m.r. spectra indicated that (**3a**) exists in the keto form. The quantum yields for disappearance of 2-NpOMe ($\sim 10^{-2}$ M) for [AA] in the range 10^{-1}—10^{-2} M



a; R = H
b; R = Me

Scheme 1

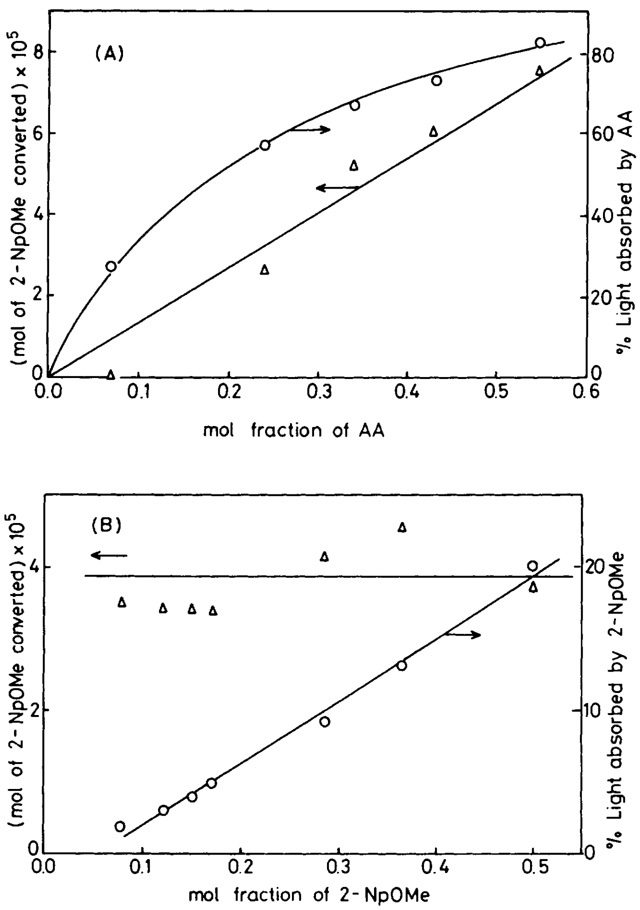


Figure 1. (A) plot of mol of 2-NpOMe reacted (△) and % of incident light absorbed by AA (○) (or by 2-NpOMe for plot B) *vs.* mol fraction of AA (or 2-NpOMe for plot B) in MeCN using Rayonet 300 nm lamps as the light source. (A) [2-NpOMe] = 5.1 × 10^{-2} M; (B) [AA] = 5.25 × 10^{-2} M.

were about 0.08 and increased as [2-NpOMe] increased. The products (**2**)—(**4**) together with their precursors were obtained in > 75% overall yields.

A plot of mol of 2-NpOMe which had reacted against mol fraction of AA for a constant concentration of 2-NpOMe of 5.1 × 10^{-2} M shows that the variation approximately parallels the percentage of light quanta absorbed by AA (Figure 1A), indicating that direct excitation of AA causes the photocycloaddition. Figure 1B shows a similar plot at a constant concentration of AA of 5.25 × 10^{-2} M and demonstrates that the excitation of 2-NpOMe does not induce the photocycloaddition. The fluorescence intensity of 1-NpOMe and 2-NpOMe is quenched by AA with k_q 3.3 × 10^{10} and 1.0 × 10^{10} dm^3 mol^{-1} s^{-1} respectively without the appearance of a new emission.† In spite of the efficient fluorescence quenching the phosphorescence intensity of NpOMe remained virtually invariable in the absence or presence of up to 0.1 M of AA. These observations confirm the pattern of energy migration within the exciplex by a 'ping-pong' mechanism, *i.e.*, ^{1}NpOR + AA → NpOR + ^{1}AA → NpOR + ^{3}AA → ^{3}NpOR + AA → emission. Triplet state xanthone (E_T 74 kcal/mol; cal = 4.184 J) failed to sensitize the photocycloaddition under the conditions where AA (E_T 72 kcal/mol) could quench 50—90% of the xanthone triplet state. The combined results rule out the possibility of these spectroscopic excited states being responsible for the photocycloaddition. Whereas AA was reported to undergo photocycloaddition to alkenes from the lowest triplet state,[13] in the present case its excited state responsible for the photocycloaddition may be one of those higher excited states that have not been identified.

The cycloaddition occurs regiospecifically with low quantum efficiency which may arise from competing isomerizations

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† Spectroscopic properties of 1-NpOMe: E_S 89.3, E_T 59.7 kcal/mol; 2-NpOMe: E_S 87.5, E_T 60.0 kcal/mol in MeCN. The E_T value of AA is calculated from the 0–0 band of the phosphorescence spectra to be 74.7 kcal/mol (383 nm) in pentane and 71.9 kcal/mol (398 nm) in alcohols; E_S of AA is estimated from the quenching of NpOMe fluorescence to be ≤ *ca.* 90 kcal/mol.

of AA.[14] The relationship between the isomerization with this and de Mayo's cycloaddition remains to be clarified.

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