[2 + 2] Photocycloaddition of Acetylacetone to Naphthoates: a Diverse Addition Pattern

Yuan L. Chow,*[a] Xiao-Yun Liu,[a] and Shengzhi Hu[b†]

[a] *Department of Chemistry, Simon Fraser University, Burnaby, B.C., Canada V5A 1S6*
[b] *Department of Chemistry, Xiamen University, Xiamen, Fujian, People's Republic of China*

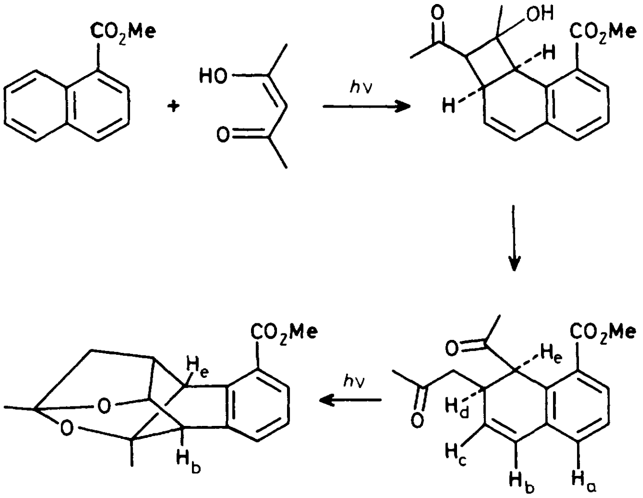
Acetylacetone photolytically adds to 1- and 2-naphthoates with or without acid catalysis by the [2 + 2] mode resulting in divergent regioselectivities; the structure of a secondary intramolecular cyclization product was ascertained by means of *X*-ray crystallography.

The [2 + 2] photocycloaddition is a versatile synthetic method for construction of carbon skeletons and has been reviewed.[1] Its utility has also attracted extensive mechanistic studies;[2] for example, current reports on enone photocycloaddition[3,4] provide much evidence for the understanding of this useful reaction. It is well documented that the photocycloaddition of the enols of β-diketones, generally known as the de Mayo reaction,[5] occurs with simple alkenes but rarely with an aromatic nucleus.[6] We now report the successful photoadditions of acetylacetone (AA) to methyl 1- and 2-naphthoates (1- and 2-NpCO_2Me) and their diverse reaction patterns.

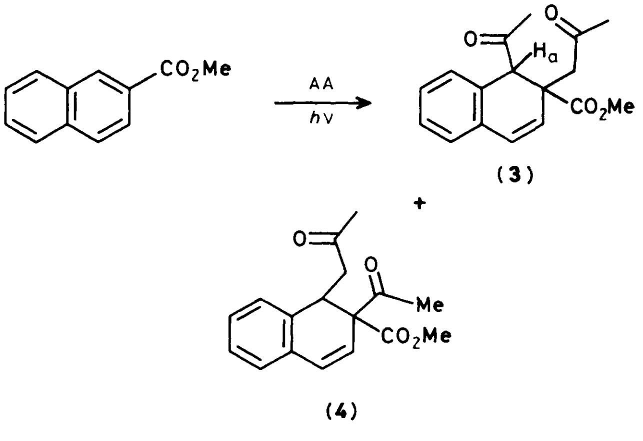
Photolysis of a mixture of 1-NpCO_2Me and AA in methylene chloride gave the diketone (**1**) which was further photolytically transformed to the 1,3-dioxane (**2**) when irradiated through a Pyrex filter. Irradiation of (**1**) with a Corex filter caused extensive Norrish Type I reaction to give methyl 7-acetonyl-1-naphthoate as a by-product. With higher [AA]/[1-NpCO_2Me] ratios, the efficiency of the diketone formation was shown to increase in parallel with the fraction of light absorbed by AA; with a 10:1 ratio, 60% of 1-NpCO_2Me was photolysed in 8 h to give (**1**) (30% isolated) and minor products; (**2**) was hardly formed because of preferential absorption by AA. The reaction pattern indicates that the excitation of AA causes the photocycloaddition but does not reveal the identity of the excited species responsible for the primary photoprocess, owing to possible energy transfer processes between reactants.[‡] No ground state complex was detected between the reactants by u.v. spectroscopy.

The structure of the diketone (**1**) was determined from spectroscopic data and the positions of the ketone side chains were confirmed by extensive ^{1}H n.m.r. studies. Nuclear Overhauser enhancement (n.O.e.) experiments showed that H_b (dd, δ 6.52) is located close to H_a (δ 7.31) and decoupling experiments revealed that H_d (m, δ 3.33) is coupled with H_c (dd, *J* 9 and 2.5 Hz, δ 5.78). The structure of the 1,3-dioxane (**2**) was determined by *X*-ray crystallography,[§] since the particular bridged structure led to n.m.r. singlets at δ 3.13 and 3.72 for H_b and H_e and other anomalies. It also confirmed the *cis*-orientation of the two ketone side chains in (**1**) so that three π-bonds can participate in photocycloaddition; such a [2 + 2 + 2] cycloaddition involving two carbonyl groups has not been demonstrated before. We believe that this is a stepwise intramolecular cyclization induced by the triplet excited styrene moiety.

Photolysis of AA with 2-NpCO_2Me (ratio 10:1) in acetonitrile caused 60% conversion in 15 h and the diketones (**3**) and (**4**) were isolated in 37 and 3% yields. Similar photoaddition in the presence of a trace amount of H_2SO_4 gave much improved yields of the diketones (**3**) and (**4**) in *ca.* 1:1 ratio; the total quantum efficiency for formation of (**3**) and (**4**) increased several fold when [H_2SO_4] increased in the range 10^{-4} to 10^{-3} M. The regiochemistry of these two products was



(**2**) (**1**)



(**3**)

(**4**)

[†] Author for crystallographic enquiries.

[‡] The E_s values for 1-NpCO_2Me and 2-NpCO_2Me were estimated from the fluorescence spectrum in methylcyclohexane to be 85.9 (λ 330 nm) and 84.5 kcal/mol (λ 338 nm) (cal = 4.184 J), and that of AA from quenching studies (ref. 6) to be ≤90 kcal/mol. Likewise E_T of 1-NpCO_2Me and 2-NpCO_2Me was determined to be 57.2 kcal/mol (500 nm) and 59.3 (482 nm) and that of AA is estimated from quenching studies to be 72—74 kcal/mol (ref. 6).

[§] *Crystal data*: $C_{17}H_{18}O_4$, triclinic, space group $P\bar{1}$, a = 7.401(1), b = 7.656(1), c = 13.882(1) Å; α = 84.75(1), β = 86.49(1), γ = 65.08(1)°, Z = 2. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo-K_α radiation. The structure was solved by direct methods, and refinement by full-matrix least-squares led to R = 0.049 for 2442 observed reflections having $I > 3\sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

resolved from their ^1H n.m.r. data. The diketone (**3**) showed a ^1H singlet at δ 4.47 for H_a and an AB quartet (δ 3.19 and 3.03, *J* 18.5 Hz) for the diastereotopic methylene protons; (**4**) exhibited a triplet at δ 4.34 and a doublet at δ 2.56 (*J* 6 Hz) for these protons. Similar acid catalysis was also observed in the photocycloaddition of AA to 1-$NpCO_2Me$. In contrast to the recently published acid effects on [2 + 2] photocycloadditions, only a trace amount of H_2SO_4 is required to cause the quantum efficiency changes in the present cases; it may imply the presence of charge transfer intermediates as reactive species.[4] The photocycloadducts (**1**), (**3**), and (**4**) are useful intermediates for ring extensions in synthesis. The mechanism of the photoaddition and the effects of sulphuric acid remain to be clarified.

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