Photocycloaddition of 2-Acetylnaphthalene to Methyl Cinnamate. A 2 + 4 Electron Photocycloaddition

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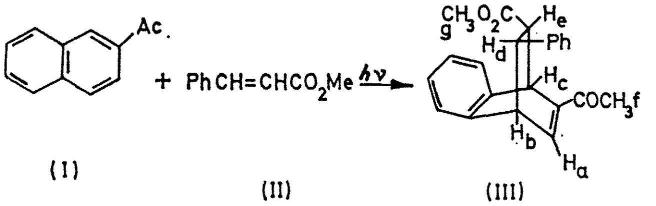
Summary Irradiation of 2-acetylnaphthalene with methyl cinnamate yields a novel 2 + 4 electron photocycloaddition product.

SEVERAL examples of photocycloaddition to, and/or photodimerization of, benzene[1] and anthracene[2] derivatives are known. In marked contrast few photochemical reactions incorporating the naphthalene moiety have been reported.[3] We have found that irradiation of 2-acetylnaphthalene (I) with methyl cinnamate (II) yields (III), a 2 + 4 election photocycloaddition product.



(I) (II) (III)

A solution of 2-acetylnaphthalene (1·8 g.) and *trans*-methyl cinnamate (8·23 g.) in diethyl ether (250 ml.) was irradiated through a Pyrex filter with a 450 w Hanovia mercury vapour lamp at *ca.* 15°. Vapour phase chromatography of aliquots from the reaction mixture indicate that the photosensitized stationary state of *cis* and *trans* methyl cinnamate (*ca.* 1 : 1) was rapidly attained; further irradiation (1 month) led to consumption of the cinnamate. The solvent was evaporated leaving a yellow oil which was chromatographed on alumina giving (III) (0·35 g.) in the ether eluent.

The combustion and mass spectral† analysis of (III) (m.p. 184—186°, from EtOH) indicate a one-to-one adduct. The i.r. spectrum shows ester carboxyl and α,β-unsaturated carbonyl groups at 1730 and 1675 cm.$^{-1}$. The u.v. spectrum is consistent with the benzenoid and α,β-unsaturated carbonyl chromophores [λ_{max} (hexane) Å (ϵ): 2770 (767), 2685 (789), and 2350sh (5520)].

The n.m.r. spectrum provides definitive proof of the gross structure of (III) and allows a tentative assignment of stereochemistry. In addition to singlets due to methyl protons at δ 3·58 (H_g) and 2·15 (H_f) and the aromatic protons between 6·80—7·43 p.p.m., the other protons can be assigned by first-order analysis to the positions indicated (III and the Table).

*Chemical shift and coupling constants for protons assigned for (III)**

		H_a	H_b	H_c	H_d	H_e
H_a	..	δ=4·51	±7·4	—	—	—
H_b	..	±7·4	δ=3·77	—	±12·3	—
H_c	..	—	—	δ=3·26	—	|8·8|
H_d	..	—	±12·3	—	δ=3·12	|2·15|
H_e	..	—	—	|8·8|	|2.15|	δ=2·78

* In CCl_4, Me_4Si as internal standard.

The relative sign information was established by irradiating the high frequency member of the vinyl (H_a) doublet and observing a sharpening of the higher frequency doublet in the H_d-quartet. Besides establishing that J_{ab} and J_{bd} have like signs, this shows the presence of an unresolved coupling between protons H_a and H_d, and the absence of

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† The analytical sample (m.p. 184—186°) was recrystallized from ethanol. 70 volts spectrum—high mass peak at 332 (parent peak). Major peaks at 155 (base peak) and 170.

coupling between the vinyl proton and either H_c or H_e. Irradiation in the aromatic region sharpens the H_d-lines, showing that the phenyl substituent is at this position. The magnitude of J_{de} suggests a *trans* configuration for these protons. These facts reduce the number of structural possibilities to two, *i.e.*, (III) and the isomer interchanging Ph–H_d and MeO_2C–H_e. We favour structure (III) because of the presence of long-range coupling J_{ad}.[4] Also, the magnitude of the three vicinal couplings involved suggests a puckered conformation of the saturated bridge such that the phenyl and carboxylate substituents are twisted further apart.[5]

While the mechanism for the formation of (III) is as yet unknown, some pertinent points should be mentioned. The initial excitation is predominantly to the n,π^* singlet of 2-acetylnaphthalene since methyl cinnamate has only weak absorption in the region of irradiation, *i.e.*, > 3000 Å; however, direct excitation of the methyl cinnamate cannot be ruled out since the reaction is so inefficient. The n,π^* singlet of 2-acetylnaphthalene usually leads to the π,π^* triplet[6] which is quenched by methyl cinnamate as indicated by the sensitization of *cis–trans* isomerization. The photocycloaddition and photo-ene reactions of methyl cinnamate to tetramethylethylene occur *via* the cinnamate singlet and not *via* the triplet.[7] No dimers of methyl cinnamate were obtained.[8] Only one isomer of (III) is observed in spite of the presence of both *cis-* and *trans*-methyl cinnamate. No thermal reaction was observed when (I) and (II) were kept at 200° for 20 hr. The u.v. spectra of mixtures of 2-acetylnaphthalene and methyl cinnamate gave no indication of absorption due to a charge transfer complex between ground state molecules.

Orbital symmetry considerations negate a concerted $\pi^2s + \pi^2s + \pi^2s$ reaction from an excited state while $\pi^2s + \pi^2s + \pi^2a$ is allowed.[11,12] Thus, (III) would originate from reaction with *cis*-methyl cinnamate. There is steric hindrance in the transition state for reaction with the *trans*-olefin which may account for the stereoselectivity of the reaction.

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