Stereodynamic Protection of a Carbonyl Group by Two Benzene Rings Against Interaction with a Triplet n→π* Quencher in the Photochemical Reaction of 5,6,7,12,13,14-Hexahydro-6,13-methanodibenzo[*a,f*]cyclodecen-15-one

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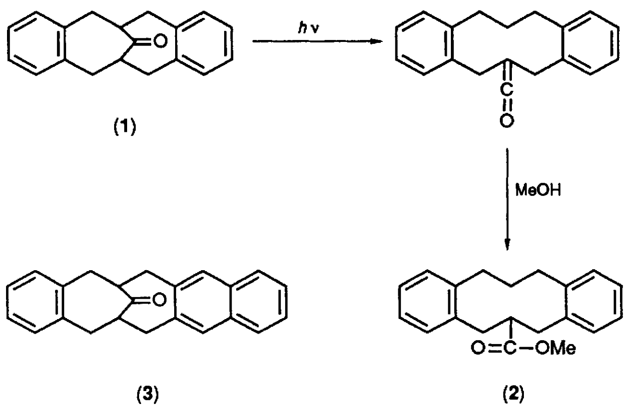
In the photolysis of the flexible 5,6,7,12,13,14-hexahydro-6,13-methanodibenzo[*a,f*]cyclodecen-15-one (**1**), the two annulated benzene rings protected the carbonyl group against interaction with a triplet quencher such as naphthalene.



(1)

(3)

(2)

Naphthalene and its derivatives have frequently been used as effective n→π* triplet quenchers in photochemical reactions of carbonyl compounds.[1] Photolysis† of the pentacyclic compound (**1**) in CH_2Cl_2 for 1 h at 5 °C and quenching of the photolysate with methanol gave the expected ester (**2**), colourless prisms, m.p. 142—144 °C (from EtOH), *via* the ketene intermediate, in 39% yield with 61% recovery of (**1**).‡ Interestingly, this photochemical reaction was not quenched by addition of naphthalene (2 mol equiv.) under the above conditions and gave a 30 : 70 mixture‡ of (**2**) and (**1**). On the

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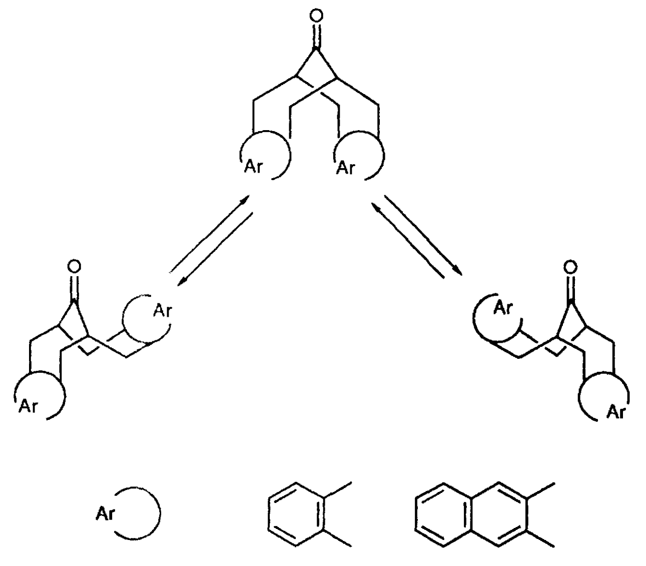
† A 30 mM solution (60 ml) of (**1**) in CH_2Cl_2 was irradiated using a 100 W high-pressure Hg lamp (Riko UVL-100HA).

‡ Determined by VPC (Yanaco G2800 with methyl silicone capillary column).



Scheme 1

other hand, the intramolecular presence of a naphthalene ring effectively quenched the photolysis of the benzo-naphtho derivative (**3**) and unchanged (**3**) was recovered quantitatively after irradiation for 1 h.

Since (**1**) was reported to invert between two chair–boat conformers at room temperature,[2] we reasoned that the two annulated benzene rings might shield the carbonyl group and the naphthalene molecule could not come close enough for energy transfer to it from the excited carbonyl group (Scheme 1). Thus, at a temperature when the inversion of (**1**) becomes slow or is frozen, naphthalene may gain access to (**1**) from the open side of the chair–boat conformer and be able to act as a quencher.

Indeed, evidence for this was obtained in the photolysis of (**1**) at −70 °C; a 37:63 mixture‡ of the product (**2**) together with (**1**) was obtained in the absence of naphthalene, while unchanged (**1**) was recovered quantitatively in the presence of the quencher (2 mol equiv.).

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References

1 L. J. Johnson and J. C. Scaiano, *J. Am. Chem. Soc.*, 1987, **109**, 5487.

2 S. Mataka, K. Takahashi, T. Hirota, K. Takuma, H. Kobayashi, M. Tashiro, K. Imada, and M. Kuniyoshi, *J. Org. Chem.*, 1986, **51**, 4618.