Dual Reaction Pathways in the Photocycloaddition of Cyclohepta-1,3,5-triene to 9-Cyanoanthracene

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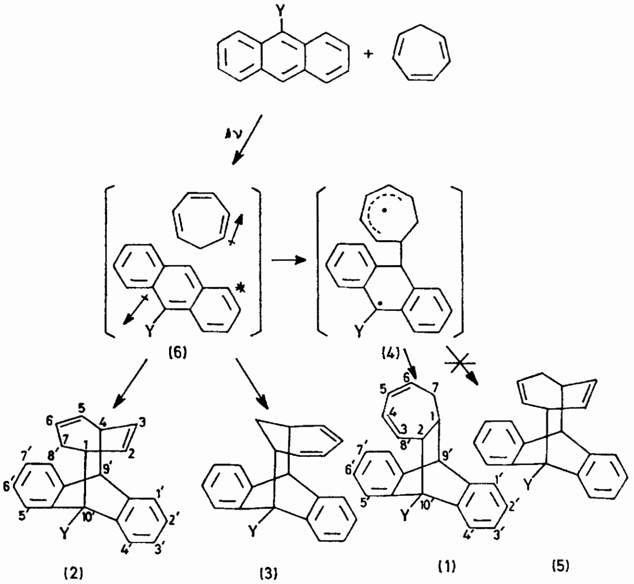
Summary The photocycloaddition of cyclohepta-1,3,5-triene to 9-cyanoanthracene yielded a $4\pi_s+2\pi_s$ adduct (**1a**) and a $4\pi_s + 4\pi_s$ adduct (**2a**) which are formed from different reaction pathways.

Photocycloadditions of conjugated polyenes to anthracene and substituted anthracenes yield a variety of interesting products.[1–5] Kaupp investigated the photocycloadditions of cyclopenta-1,3-diene and cyclohexa-1,3-diene to anthracene and suggested a common biradical precursor to both the $4\pi_s + 2\pi_s$ and $4\pi_s + 4\pi_s$ adducts.[4] Subsequently Sasaki and his co-workers studied the photocycloaddition of cyclohepta-1,3,5-triene to anthracene and proposed a common biradical precursor to both the $4\pi_s + 4\pi_s$ (**2b**) and $4\pi_s + 6\pi_s$ (**3b**) adducts.[5] Our recent work indicated that these photocycloadditions may proceed *via* exciplex intermediates,[6] and the reaction pathways may be influenced by the nature of the exciplex intermediates involved.[3] We report now the photocycloaddition of cyclohepta-1,3,5-triene to 9-cyanoanthracene. The results suggest that the $4\pi_s + 2\pi_s$ adduct (**1a**) and the $4\pi_s + 4\pi_s$ adduct (**2a**) are formed from different reaction pathways.

A 0·02 M solution of 9-cyanoanthracene in benzene containing cyclohepta-1,3,5-triene (0·56 M) was irradiated with a Hanovia 450 W Hg-arc and a uranyl glass filter (340 nm cutoff) until 9-cyanoanthracene was consumed. Three 1 : 1 adducts were isolated by chromatography on silica gel, (**1a**), m.p. 157—158 °C (37%), (**2a**), m.p. 144—145 °C (25%), and (**3a**), m.p. 115—116 °C (4%), all of which have been characterized by elemental and spectroscopic analyses. Traces of two other adducts were also detected in the reaction mixture. The structures of adducts were established unambiguously by high resolution n.m.r. spectroscopy at 270 MHz with spin decoupling. The 1-H, of (**1a**) was found to be coupled with each 7-H and 2- and 9′-H; 4-H of (**2a**) was found to be coupled with 3-, 5-, and 9′-H, and 1-H with 2-H and each 7-H. Compound (**3a**) was identified to be the $4\pi_s + 6\pi_s$ adduct.

Since the fluorescence of 9-cyanoanthracene is efficiently quenched by cyclohepta-1,3,5-triene ($k_q \tau$ 34 ± 2 mol^{-1} l), the photocycloaddition must proceed predominantly *via* the singlet excited state of 9-cyanoanthracene. Concerted $4\pi_s + 4\pi_s$ photocycloadditions are symmetry-allowed processes, while $4\pi_s + 2\pi_s$ photocycloadditions are symmetry-forbidden processes but may proceed by a stepwise mechanism *via* polar exciplexes and biradical intermediates.[3,7] 9-Cyanoanthracene reacts photochemically with cyclic 1,3-dienes to give the $4\pi_s + 4\pi_s$ adduct as the only isolated product,[1,8] while it reacts with cyclohepta-1,3,5-triene to give a mixture of adducts. The formation of (**1a**) may be rationalized *via* the most stable biradical precursor (**4a**). However, 1,4-cyclization of (**4a**) will not give (**2a**) but (**5**) instead which contains the CN group and the CH_2 group in the opposite orientation. The results clearly indicate that (**1a**) and (**2a**) are formed *via* different pathways and may be explained by invoking an exciplex intermediate (**6a**). The CN group in (**6a**) will orient in the same direction as the CH_2 group in order to have the most favourable dipole interaction. The exciplex (**6a**) may collapse either *via* a concerted $4\pi_s + 4\pi_s$ addition to give (**2a**) or in a stepwise manner to give the most stable biradical precursor (**4a**) which subsequently cyclizes to give (**1a**). Although we have not been able to characterize the exciplex (**6a**) as yet, it may conceivably be more polar than the 9-cyanoanthracene–1,3-diene exciplexes[6] owing to the presence of additional conjugation in the triene. Thus (**6a**) may decay *via* both the concerted addition and the biradical intermediate.[3]



a; Y = CN
b; Y = H

While (**1a**) is the major product in the photocycloaddition of the triene to 9-cyanoanthracene, the $4\pi_s + 2\pi_s$ adduct (**1b**) is not formed in the addition to anthracene.[5] If biradical (**4b**) is the intermediate in the anthracene reaction, the formation of a certain amount of (**1b**) would be expected. Therefore, the biradical (**4b**) may not be the precursor to the $4\pi_s + 6\pi_s$ adduct (**3b**) from anthracene and the triene.

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