Polar Substituents in Pericyclic Reactions: Photochemistry of 2-Cyanobenzobarrelene

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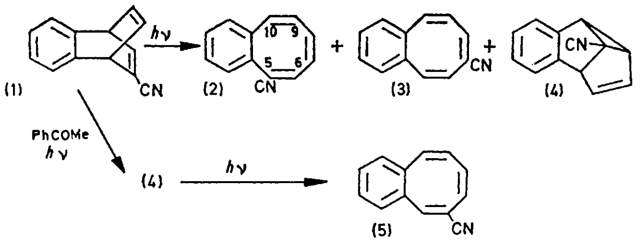
Summary Deuterium labelling studies show that 7-cyanobenzocyclo-octene, the major product from the direct irradiation of 2-cyanobenzobarrelene, derives from initial $2_\pi + 2_\pi$ bonding between the vinyl and vinylcyano units.

Interest in the effects of polar substituents on pericyclic processes has been heightened recently by the configuration-interaction calculations of Epiotis[1] which indicate that for some polar $4n$ systems reaction in *anti*-Woodward–Hoffmann[2] mode may occur. We report here the powerful influence of the cyano-group on the mechanistic course of the photochemical transformation of benzobarrelene into benzocyclo-octene.

2-Cyanobenzobarrelene (**1**)† was prepared by the treatment with CuCN of 2-bromobenzobarrelene, isolated from the addition of benzyne to bromobenzene. Direct irradiation (450-W medium-pressure Hanovia lamp; Corex filter; cyclohexane) of (**1**) led cleanly to three isomeric primary photoproducts: (**2**) (17%), (**3**) (54%), and (**4**) (29%). Under similar conditions, direct irradiation of (**4**) gave (**5**). Upon triplet sensitization (Pyrex filter, acetophenone), (**1**) yielded only (**4**). Thus (**2**) and (**3**) seem to derive from the singlet excited state of (**1**).



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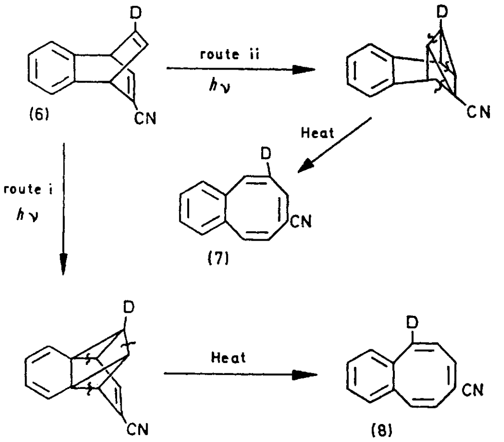
† All new compounds were characterized by i.r., u.v., and n.m.r. spectra, and gave combustion analyses in agreement with the proposed structures.

The photochemical formation of cyclo-octenes from barrelenes is generally considered to proceed *via* an initial concerted $2_\pi + 2_\pi$ cycloaddition (*e.g.*, Scheme).[3]



Scheme

Whereas there is only one possible $2_\pi + 2_\pi$ cycloaddition route to (**2**), that involving initial bridging between the benzo- and vinylcyano-units, (**3**) could be formed *via* two concerted pathways: initial benzo–vinyl bridging (route i, Scheme) or initial vinyl–vinylcyano-bridging (route ii). In order to distinguish between these two possibilities the deuterium labelled material [(**6**) 93% $^2H_1$] was synthesised from *para*-deuteriobromobenzene and irradiated directly. The n.m.r. spectrum of the deuteriated 7-cyano-product revealed that it was exclusively the β-labelled compound (**7**). Thus only the vinyl–vinylcyano-route is used in the formation of (**3**) from (**1**).

The presence of the cyano-group in the vinyl bridge of benzobarrelene dramatically changes the initial bonding preference. For benzobarrelene itself Zimmerman and his co-workers[3] have shown that the benzo–vinyl bonding pathway predominates to the extent of 94 ± 2%. In the present case benzo–vinyl bridging is now the minor pathway, and that exclusively to the substituted vinyl unit. The $2_\pi + 2_\pi$ photocycloadditions of (**1**) are thus not controlled by the polar *AX* mechanism.[1] Epiotis has reasoned that for *AX* $2_\pi + 2_\pi$ processes, reaction from the first singlet excited state should show $s + a$ stereoselectivity. Consequently, for the rigid barrelene system, where geometry demands $2_\pi + 2_\pi$ cyclizations to occur only in the $s + s$ mode, bonding to the polar vinylcyano-bridge should be the least favoured.

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[3] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, 1969, **90**, 6096.