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THE PHOTOCHEMISTRY OF CONSTRAINED NON-CONJUGATED ARENE-ETHENE BICHROMOPHORIC SYSTEMS

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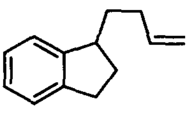
Summary. The intramolecular *meta* photocycloaddition of bichromophores **1-3** is examined and the observed regiochemistry of cycloaddition is rationalised in terms of stabilisation of zwitterionic intermediates and the steric constraints introduced into the 5-phenylpent-1-ene skeleton by the benzylic tether.

The intramolecular *meta* photocycloaddition of 5-phenylpent-1-ene derivatives has recently been used elegantly as the key step in the synthesis towards polyquinanes[2] and fenestranes.[3] Access to the latter type of compounds and other tetracyclic ring systems can, in principle, be achieved directly from the bichromophoric systems **1-3**. We have recently reported[4] the effects of introducing constraints onto the ethene moiety of 5-phenylpent-1-ene,[5] as well as substitution in the ethene, the arene and the interconnecting unit on the mode and efficiency of cycloaddition. To date, however, the effect of constraint between the benzylic and *ortho* positions of this bichromophore has not been reported. We present herein our findings on the photochemistry of such systems.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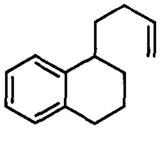
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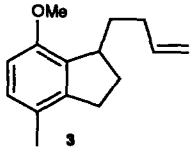

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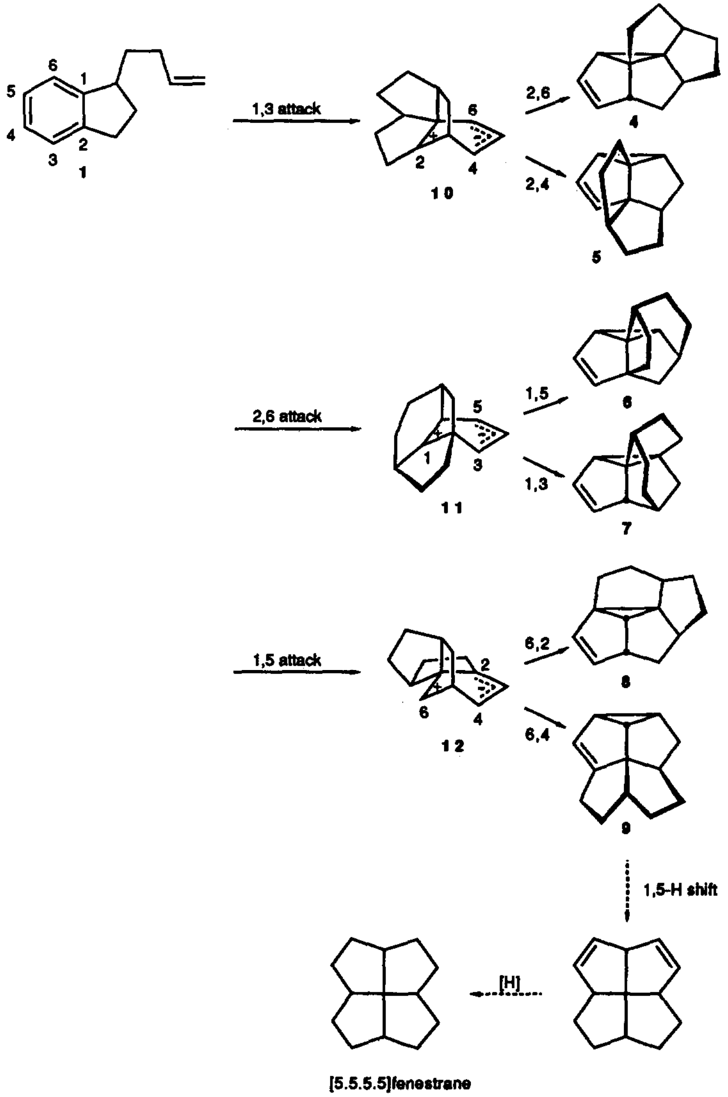
Irradiation (254 nm) of **1** as a 2% (w/v) solution in cyclohexane caused the rapid disappearance (ϕ=0.7) of the bichromophore and the clean formation of two intramolecular adduct isomers (M^+=172 mu) in an approximately 1:1 ratio (relative retention times to **1** on C20M of 0.36 and 0.50). The adducts were separated in >99% purity by preparative gc. The ^{1}H nmr data are wholly in accord with structures **4** and **5**.[6] Molecular models indicate that of the six possible adducts derived from the three possible modes of attack (Scheme 1) those having structures **6** and **7** are highly strained and would not survive the separation procedure.[5] Furthermore, the nmr spectra of both adducts show the presence of two olefinic protons, and, in both cases, the lowest field proton (assigned to H_3) is vicinally coupled to the other olefinic proton and to H_2: these data discount adducts with structures **8** and **9**.



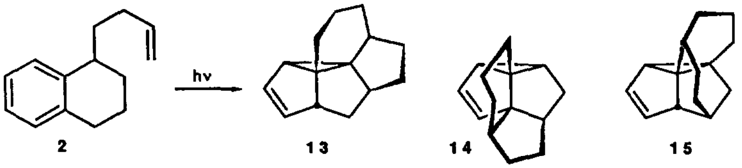
Scheme 1. The possible modes of *meta* photocycloaddition of indane 1

The sole formation of **4** and **5** can be accounted for in terms of the stabilisation of intermediates by substituents and the structural strain of the resulting adducts. Assuming that the proposed intermediate of *meta* photocycloaddition is polarised, as postulated for some other systems,[7] then the cationic centres of the respective intermediates **10** and **11** from 1,3- and 2,6-reaction of **1** are both stabilised by alkyl substitution, whereas the allylic anion in **12**, formed from a 1,5 attack, is destabilised by the substituent: such 1,3 attack has also been observed in the photoreactions of *o*-methyl- and *o*-methoxy-5-phenylpent-1-ene.[4]

The observed efficiency and specificity of the mode of attack of indane **1** are noteworthy and make this process a most attractive route to the synthesis of tetracyclo[5.5.1.$0^{2,6}0^{10,13}$] and [6.3.$2^{1,7}$0.$0^{4,8}$]tridecanes.

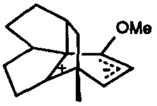
In order to assess if the specificity for the 1,3 attack in **1** is indeed a result of the relative stabilities of intermediates and/or a reflection of structural strain of the adducts, we have examined the photochemistries of **2** and **3**.

The irradiation (254 nm) of **2** (2% w/v solution in cyclohexane) proceeded at approximately half the rate of **1** and gave three adduct isomers (M^+=184 mu) in a ratio of 1.0:3.7:1.5 (relative retention times to **2** on dimethyl siloxane of 0.58, 0.60, and 0.89, see Scheme 2). The major adduct was assigned structure **13** on the basis of its ^1H nmr spectrum and comparison with the ^1H nmr spectrum of **4** [eg. the pertinent features are a dd at 5.6 ppm (H_3) showing couplings to H_2 and H_4; a ddd centred at 5.38 ppm (H_4) and a br t centred at 2.95 ppm (H_5)]. The minor isomer could not be isolated free from **13** but the ^1H nmr spectrum suggests that this is isomer **14** which, like **13**, is the product of a 1,3 reaction of the chromophores. It is surprising that the proportions of the two adducts for this mode of attack should differ so markedly from those observed for the indane derivative **1**. However, small differences in the energies of alternative reaction pathways can result in large differences in product ratios. The product with longest retention time was thermally labile under the conditions of isolation, nonetheless it was evident from the ^1H nmr spectrum that this photoisomer was unsubstituted at the 2-, 3-, 4-, and 5-positions of the dihydrosemibullvalene skeleton. [Pertinent nmr data: H_3, 5.70 ppm, dd, couplings to H_2 and H_4; H_4, 5.40, ddd, couplings to H_2, H_3, and H_4; H_5, 2.80 ppm, multiplet]. Of the remaining six isomers resulting from the three possible modes of attack only **15**, derived from 2,6-attack, has these structural features, hence the photoisomer is tentatively assigned structure **15**. In view of the apparent structural strain in **15** its thermal lability is not surprising (such thermal lability has been noted in other less strained 2,6-cycloadducts[4,5]).



Scheme 2. The products from the irradiation of tetralin 2

The above data lead us to predict that the methoxy indane **3** would have markedly different photochemistry from both **1** and **2** as it suffers from the same steric constraints as that of **1** (hence we would predict that 2,6-attack via intermediate **18** would not occur), yet intermediates **16** and **17** differ *electronically* from **10** and **11**: the methoxy group destabilises the allylic anion of **16**, whereas it stabilises the cationic centre of **17**. However, molecular models indicate that the products arising from intermediate **17** are very strained, thus we would not expect photocycloaddition of **3** to occur. This indeed is the case. (No monomeric products could be detected by gc, tlc or nmr)



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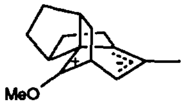

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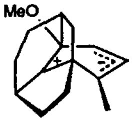

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In conclusion, the photocycloadducts of **1** and **2** are derived from orientations of attack which produce intermediates stabilised by alkyl substituents. The change from a five to a six member ring fused onto the arene and the consequent relaxation at the benzylic position in the chromophore, markedly affects the efficiency and mode of ethylenic attack onto the arene, and the position of cyclisation in the reaction intermediate. The methoxy substituent does not circumvent the dictates which the benzylic constraint places upon these indane bichromophoric systems. These aspects are being considered in synthetic uses of these systems and will be reported in due course.

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1. Address correspondence to this author at Physiology Department, University of Pennsylvania, Philadelphia, PA 19104-6085, USA.
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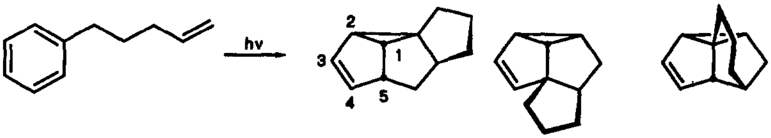
4. G.C.R. Ellis-Davies, A. Gilbert, P. Heath, J.C. Lane, J.V. Warrington and D.L. Westover, *J. Chem. Soc., Perkin Trans. 2* **1984**,1833.
5. The photocycloaddition/dearomatisation of this molecule, which is to be considered the "basic n=3" arene-ethene bichromophoric system, occurs via both 2,6- and 1,3-attack, to give three products:



cf. A. Gilbert and G.N. Taylor, *J. Chem. Soc., Perkin Trans 1* **1980**,1761. The numbering of the protons in the *photoproducts* used throughout this text is that shown above; it should be noted that it differs from that used to define regiochemistry of cycloaddition.

6. **4** ^{1}H nmr δ 5.74 (1H, dd, J's=5.6 & 2.4 Hz) 5.50 (1H, ddd, J's=5.8, 2.5 & 1.0 Hz) 2.95 (1H, br t) 2.30-2.6 (1H, m) 2.16-2.00 (4H, m) 2.00-1.60 (4H, m) 1.45-1.20 (4H, m). $C_{13}H_{16}$ requires M^+ 172.1256, found 172.1258. **5** ^{1}H nmr δ 5.59 (1H, dd, J's=5.3 & 2.0 Hz) 5.49 (1H, br d, J=5.3 Hz) 2.48 (1H, m) 2.30-2.04 (3H, m) 2.04-1.75 (5H, m) 1.75-1.52 (5H, m). $C_{13}H_{16}$ requires M^+ 172.1256, found 172.1251. Analysis of the crude reaction mixture after complete disappearance of **1** by ^{1}H nmr indicated the exclusive presence of photoproducts **4** and **5**.
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