

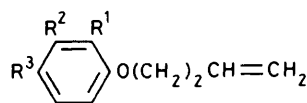
Specific Intramolecular *ortho* Photocycloaddition of Substituted 4-Phenoxybut-1-enes

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Cyano and methoxycarbonyl substituted 4-phenoxybut-1-enes undergo specific intramolecular *ortho* photocycloaddition: the primary photoadducts are thermally labile and yield cyclo-octatrienes which give bicyclo[4.2.0]octa-2,7-dienes in a facile secondary photoreaction.

We have recently discussed the substituent and structural features of arene-ethene bichromophoric compounds which influence the efficiency and mode of their photochemical reactions.¹ With very few exceptions the preferred reaction is intramolecular *meta* photocycloaddition, and this reaction with 5-phenylpent-1-ene derivatives continues to be elegantly used in the synthesis of polyquinanes² and fenestranes.³ In contrast, phenoxy-ethenyl bichromophores undergo inefficient *meta* cycloaddition and yield polymeric material on irradiation at 254 nm.¹ We have now, however, observed that, in marked contrast to the corresponding intermolecular systems with anisole derivatives,^{4,5} the presence of electron acceptor substituents on the aryl moiety of 4-phenoxybut-1-ene has a profound effect on the mode and efficiency of the photochemical reaction. The report of these novel findings from the 254 nm radiation of the bichromophores (**1**) is further prompted by the recent account by Wagner and Nahm of the photo-initiated (313 nm) intramolecular *ortho* cycloaddition of 2- and 4-(3-butenoxy)-aceto- and valero-phenones: the primary photoadduct is thermally labile and quantitatively converted into cyclo-octa-1,3,5-trienes.⁶



- (**1a**), R¹ = R² = H, R³ = CN
b, R¹ = CN, R² = R³ = H
c, R¹ = R² = H, R³ = CO₂Me
d, R¹ = R³ = H, R² = CN

Irradiation of 1% w/v solutions of the 2- and 4-substituted 4-phenoxybut-1-enes (**1a–c**) in cyclohexane under air led to the rapid formation of a yellow colouration and the slow conversion of the bichromophore into two isomers in a ratio that was markedly dependent on the proportion of (**1**) in the reaction mixture. For example, the two isomers from (**1a**) at 10% conversion of the bichromophore were present in a ratio of 3 : 2 (order of elution on non-polar g.c. columns) but at total consumption the corresponding ratio was 1 : 18. The photolabile isomer was isolated as a yellow oil by flash chromatography of the reaction mixture at 50% conversion of the bichromophore and was identified as the cyclo-octatriene (**2**) from its spectral data and their comparison with those described in ref. 6. Irradiation of (**2**) gave the photostable isomer which could be partly reverted by heating at 175 °C for 5 min: longer periods of exposure resulted in polymer formation. The photostable isomer (m.p. 78–79 °C) was assigned structure (**3**) on the basis of spectroscopic evidence[†] and this was confirmed by X-ray crystallographic determination of a single crystal.[‡] The structure consists of discrete molecules of (**3**) as shown in Figure 1.

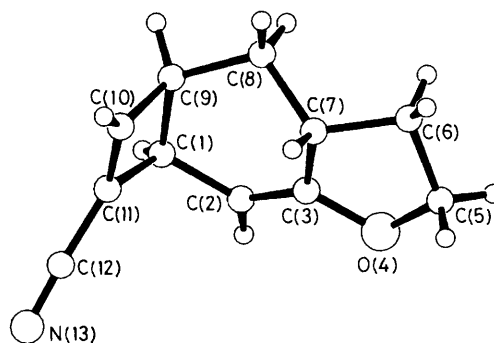
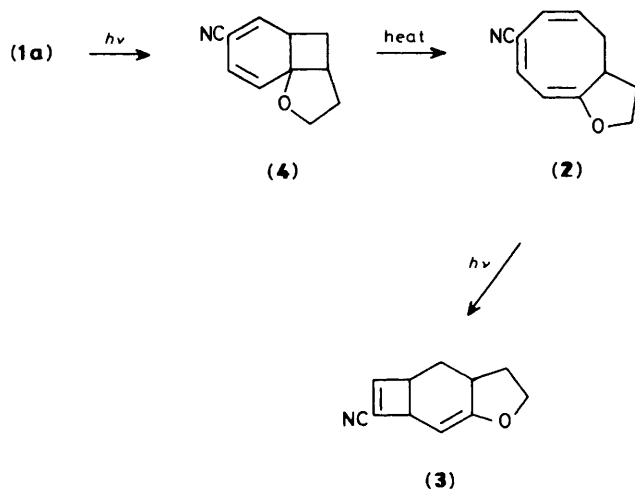


Figure 1. Molecular structure of (**3**).



[†] All compounds described here gave satisfactory analytical data. ¹H N.m.r. (C₆D₆) (**3**): δ 6.00 (br. d, H-10, J_{9,10} 1.1, J_{2,10} 0.5 Hz), 4.89 (br. dd, H-2, J_{1,2} 5.0, J_{2,7} 2.5, J_{2,6} 1.0 Hz), 3.78 (overlapping br. dds, H-5', J_{5,5'} 9.0, J_{5',6'} 9.0, J_{5',6} 1.0, J_{5',7} 0.5 Hz), 3.50 (m, 8 lines, H-5, J_{5,6'} 12.0, J_{5,6} 5.5 Hz), 3.20 (d of dd, H-1, J_{1,9} 4.0, J_{1,7} 1.0 Hz), 2.56 (m, 10 lines, H-9, J_{8',9} 6.0, J_{8,9} 2.0 Hz), 1.76 (br. m, H-7, J_{7,8'} 11.5, J_{7,8} 5.5 Hz), 1.50 (m, H-6 and H-8, J_{6,6'} 20.0, J_{8,8'} 13.0 Hz), 1.08 (m, 8 lines, H-6'), and 0.64 (m, 8 lines, H-8'); i.r.: ν_{max} (Nujol mull) 2220 cm⁻¹.

[‡] Crystal data for (**3**): C₁₁H₁₁NO, orthorhombic, space group P2₁2₁2₁, a = 10.783(8), b = 6.868(9), c = 12.183 (10) Å, U = 902.3 Å³, D_c = 1.27 g cm⁻³, F(000) = 368, Z = 4, λ (Mo-K_α) = 0.7107 Å, μ = 1.98 cm⁻¹. 619 Independent reflections above background [I > 2σ(I)] were measured on a diffractometer; the structure was determined by direct methods and refined (O,N,C anisotropic, H isotropic in fixed positions) to R 0.068 (R_w 0.070). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The primary photoisomer of (**1a**) which is the logical precursor of (**2**) is the intramolecular *ortho* cycloadduct (**4**). Evidence for this isomer in 50% converted bichromophore reaction mixtures was obtained from ^1H n.m.r. spectroscopy and by isolation of its *N*-phenylmaleimide Diels–Alder adduct but attempts to separate (**4**) chromatographically were unsuccessful. The rate of formation of the isomers from (**1a**) was increased approximately five-fold in polar solvents which is consistent with other *ortho* cycloaddition processes of ethenes to arenes,⁷ but the absence of any significant effect on the reaction rate of irradiated solutions degassed under xenon leaves open the question of the involvement of singlet or triplet intermediates in these processes.⁸

The 2-cyano isomer (**1b**) and the 4-methoxycarbonyl compound (**1c**) reacted in the same manner but at approximately half the rate of (**1a**) under similar irradiation conditions. In contrast the 3-cyano isomer (**1d**) was essentially photostable and prolonged irradiation produced small amounts of polymeric materials. Based on the corresponding intermolecular reactions of cycloalkenes and cyanoanisoles,^{4,5} both the 3- and 4-isomers (**1d**) and (**1a**) would be predicted to undergo *meta* (2,6-) cycloaddition while the 2-isomer may be expected to be relatively photostable. Thus the present observations, particularly the specific intramolecular *ortho* cycloadditions of the 2- and 4-cyano-bichromophores are contrary to the previously described influences for arene photoaddition reactions and further, the formation of the secondary photoproduct (**3**) is unprecedented in benzene photochemistry. The present photoreaction may be con-

sidered as a convenient synthetic route to the tricyclic ring system (**3**) since although the quantum efficiency of the overall process is low (*ca.* 0.05) chemical yields are of the order of 85% and gramme quantities of the stable photoisomer are readily accessible from 24 h irradiations with two 30 W low pressure mercury arc lamps.

We are grateful to Professor Wagner for communicating his results to us prior to publication on the thermal and photolabilities of the intramolecular adducts of the aceto- and valero-phenones.

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