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meta/1,4-Photoaddition of a 1,3-Diene to Benzene

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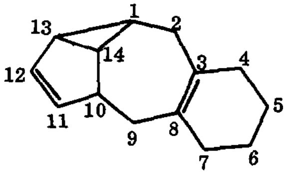
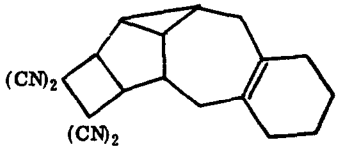
Although there are experimental[1] and theoretical[2] grounds to believe that the ground state conformation of a 1,3-diene can determine its mode of photoaddition to benzene, previous studies have been complicated by the use of acyclic dienes which are conformationally flexible. We now report the photoaddition to benzene of two conformationally fixed 1,3-dienes.

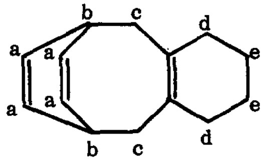
Irradiation (low pressure mercury arc, 6-w at 254 nm ; 20° ; air or N_2 ; 24 h.) of a mixture of benzene (100 ml.) and 1,2-dimethylene cyclohexane (30 ml.) gave, after vacuum distillation (120°, 0.1 mm Hg) of the combined products from four such preparations, 2.0 g. of a colourless oil which largely comprised two 1:1 photoadducts (m.s. - g.l.c., Carbowax 20M : $\Phi_{\text{total}} = 0.06$) A and B in the ratio 1:2.5 respectively. An n.m.r. spectrum of the distilled mixture showed no significant resonances attributable to the group $= CH_2$, so both ethylenic moieties of the <u>cis</u> 1,3-diene are involved in the two photoadducts. Adduct A was obtained in 95% purity by preparative g.c. [the only contaminant being compound B], and its chemical and spectroscopic properties show that it is the novel 1,4-1',3'-benzene cycloadduct (1). Thus it was unreactive towards maleic anhydride and N-phenylmaleimide. Tetracyanoethylene gave a 1:1:1 adduct (m.p. 152 - 154° dec) in low yield : this is assigned structure (2) by analogy with the behaviour of closely related systems.[3] The n.m.r. spectrum of A is fully consistent with structure (1) [5.55 (2H, br s, H-11, H-12), 3.0 - 3.3 (1H, m, H-10), 2.25(3H, m, H-2, H-14), 1.85 (7H, m, H-1, H-4, H-7, H-9) and 1.55 p.p.m. (5H, m, H-13, H-5, H-6)]. The i.r. spectrum shows structurally significant peaks at 1600 (C=C stretch in small-ring olefin) and 1010 cm^{-1} (probably cyclopropane ring) which further support the structure (1). The u.v. spectrum in cyclohexane showed $\lambda_{\text{max.}}$ 220 nm, $\epsilon = 5000$ l mol^{-1} cm^{-1}, consistent with the vinylcyclopropane chromophore. Adduct B was obtained in > 95% purity by extraction of the oil with aqueous silver nitrate and treatment of the crystalline complex with aqueous ammonia. The assignment of a 1,4-1,'4'-structure (3) follows clearly from the n.m.r. spectrum which showed resonances at 5.90 (4H, t, Ha, $J_{a,b} = 4.0$ Hz), 2.85 (2H, m, Hb), 2.40 (4H, br s, Hc), 1.80 (4H, m, Hd), and 1.50 p.p.m. (4H, br t, He, $J_{d,e} = 3.0$ Hz). Spin decoupling experiments substantiated this assignment.



(1)



(2)



(3)

In contrast with the behaviour of the above cis- diene, photoreaction of the rigidly trans 3-methylenecyclohexene with benzene under comparable conditions gave very low yields of a complex mixture containing at least four 1:1 adducts, a diene dimer, and traces of aromatic products. Although none of these has yet been definitely identified, there was some evidence for 1, 2-cycloaddition to the benzene ring, and the survival of a $=CH_2$ group in at least one adduct.

Although we have as yet no definite information on the nature or multiplicity of the excited state precursor(s) of adducts (1) and (3), other photoadditions between benzene and alkenes[4] or 1, 3-dienes[5] involve S_1 benzene. It may be noted that the 1, 4-1', 3' cycloaddition of cis- buta-1, 3-diene to benzene has been predicted to be allowed as a concerted process from either S_1 diene or S_1 benzene.[6]

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