Photoaddition of Allenes to Benzene

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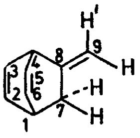
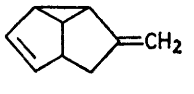
Summary Allene and cyclonona-1,2-diene undergo light-induced 1,3- and 1,4-cycloaddition to benzene; the latter mode of reaction predominates in both cases.

Simple mono-olefins are known to undergo unsensitised 1,2-, 1,3-, and 1,4-photochemical cycloaddition to benzene.[1–5] In all reported examples, the 1,4-addition reaction is a minor process and has a Φ value which is of the order of one ninth or less that of the 1,3-reaction.[3,5] The 1,2-photoadducts are formed with Φ values of 0·1—0·5, but undergo ready photo-dissociation, so only traces are normally obtained.[3] With 1,3-dienes and benzene, the major photoadducts result from initial 1,4-, 1,4′-cycloaddition.[6] We now report the photoreactions of two 1,2-dienes with benzene.

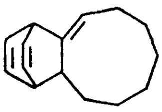
Irradiation (254 nm) of a 5% v/v solution of allene in benzene under nitrogen at 25 °C gave a very low yield of four 1:1 adducts in the approximate ratio 1:2:6:12. This ratio was invariant with time although prolonged irradiation did yield small amounts of a 2:1 allene–benzene adduct seemingly at the expense of the major 1:1 adduct. The two most abundant adducts have been isolated by preparative g.l.c. and the major of these is assigned the 1,4-adduct structure (**1**) on the basis of the following spectroscopic evidence. The u.v. spectrum (n-hexane) of



(1)



(2)



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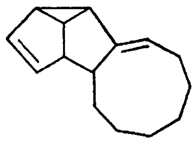

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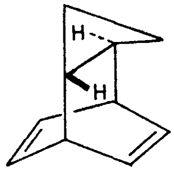

(5)

the compound has λ_{max} 216 nm and significant absorptions in the i.r. spectrum are observed at 3050, 2950 (satd. and unsatd. C–H stretch, 1650, 1590 (terminal olefin, olefin in bicyclo[2,2,2]octadiene), 870 (terminal olefin), and 710 cm^{-1} (*cis*-disubst. olefin). The n.m.r. spectrum unambiguously confirms structure (**1**) [τ 3·6—3·9 (4H, t, $J_{1,2} = J_{1,6} = J_{3,4} = J_{4,5} = J_{1,3} = J_{1,5} = J_{2,4} = J_{4,6} = 3{\cdot}7$ Hz, 2-, 3-, 5-, 6-H), 5·2—5·6 (2H, 2 × br. s, 9-, 9′-H, $J_{9,9'}$ 1 Hz), 6·0—6·3 (1H, m, 4-H), 6·3—6·5 (1H, m, $J_{1,7}$ 2·5 Hz, 1-H), and 8·0—8·1 (2H, q, $J_{7,9} = J_{7,9'} = 2$ Hz, 7-H)]. In the mass spectrum the adduct readily breaks down to its original components. The spectroscopic properties of the other major product are consistent with its assignment as a 1,3-adduct (**2**) with the exocyclic double bond in conjugation with the cyclopropane ring.[1,2] The two adducts (**1**) and (**2**) are not interconverted by light under their conditions of formation.

Similar irradiation of a 10% v/v solution of cyclonona-1,2-diene in benzene gave principally two 1:1 adducts in a 1:4 ratio which was again invariant with time. As with allene, the major product was shown from spectroscopic data to have a 1,4-structure (**3**), and the minor adduct (**4**) resulted from 1,3-cycloaddition.

The present reactions are the first reported examples in which a hydrocarbon olefin undergoes unsensitised 1,4-cycloaddition to benzene as the major process.† Srinivasan has reported the 1,4-cycloaddition of cyclobutene to benzene as a minor process but did not comment on the stereochemistry.[5] A concerted addition *via* $^1B_{2\mu}$ benzene would be expected on orbital symmetry grounds to have the highly strained *trans*-structure (**5**).[8] We have observed that the cyclobutene–benzene 1,4-adduct is oxidised by concentrated nitric acid to cyclobutane-*cis*-1,2-dicarboxylic acid. Thus the addition seems to be non-concerted, perhaps because excessive strain would be involved in a concerted process.

It had been hoped to use the 1,3-addition of allenes to benzene as a route to semibullvalenes *via* base-catalysed migration of the exocyclic ethylenic bond into the rings, but the 1,3-adducts proved stable to bases, reflecting perhaps the negligible 'aromatic' stabilisation in semibullvalenes,[9] or lack of formation of the carbanion.

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† The sensitised 1,4-cycloaddition of dichlorovinylene carbonate to benzene has recently been reported.[7]

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