

THE EFFICIENT, HIGHLY SELECTIVE PHOTOCYCLOADDITION OF
2, 3-DIHYDROPYRAN TO BENZENE

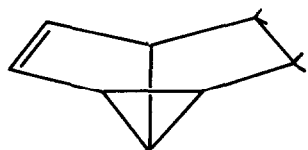
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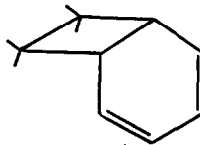
(Received 30 November 1976; received for publication 6 January 1977)

The 254 nm irradiation of benzene in the presence of ethylenes which have ionisation potentials less than ca. 9.1 eV yields either exo and endo 1,3-cycloadducts (1) or a mixture of 1,2- (2) and 1,3-cycloadducts.¹ Although the quantum yields of the two cycloaddition reactions vary for different systems, the ratio $\frac{\phi_{1,2-}}{\phi_{\text{other products}}}$ tends to increase with decrease in the ethylene ionisation potential: the highest reported value for this ratio which is a convenient measure of the selectivity of the reaction is four and observed for the addition of 2,3-dimethylbut-2-ene (ionisation potential 8.3 eV) to benzene.¹ We now describe the stereospecific light-induced cycloaddition of 2,3-dihydropyran (ionisation potential 8.34 eV) to benzene which is outstanding (a) for the very high selectivity of the 1,2-cycloaddition pathway compared with the earlier reported systems involving donor ethylenes^{1,2} and (b) for a quantum efficiency greater than those previously observed for any mode of addition of an ethylene to benzene.

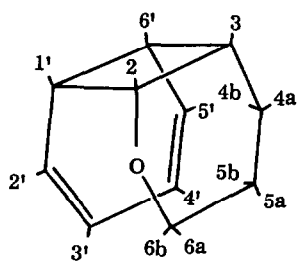
Irradiation (low pressure Hg lamp, 20° C, air or N₂) of a solution of benzene and 2,3-dihydropyran either alone or with a diluent yielded essentially three 1:1 adducts (m. s./g. c. M⁺ = 162), the relative amounts of which were time, solvent and concentration dependent. One adduct, however, always predominated and was isolated in > 98% purity by preparative g. c. The 1,2-endo cycloadduct structure (3) is assigned to this major product on the basis of the following spectroscopic and chemical data. The u. v. spectrum showed λ_{max} (cyclohexane) 208 nm (ϵ 1.8 x 10³ l mol⁻¹ cm⁻¹) and 275 nm (ϵ 1.5 x 10³ l mol⁻¹ cm⁻¹) and the i. r. spectrum had major absorptions at 3020, 2920, 2840, 1580, 1110, 1050, and 715 cm⁻¹. Complete identification of the adduct as (3) was afforded by its 220 MHz n. m. r. spectrum (C₆D₆) which had resonances at δ 5.68 (4H, m, H_{2'}, 3', 4' and 5'), 4.34 (1H, q, H₂, J_{1',2} = 5.8 Hz, J_{2,3} = 3.4 Hz and J_{2,6'} = 0.7 Hz),³ 3.63 (1H, dbl. d, H_{6a}, J_{6a,5b} = 5Hz, J_{6a,5a} = 2Hz), 3.20 (1H, m, H_{6b}, J_{6a6b} = 11 Hz), 3.04 (1H, q, H_{1'}), 2.83 (1H, dbl. d, H_{6'}), 2.60 (1H, dbl. d, H₃) 1.46 (3H, m, H_{4a, 4b and 5a}) and 1.18 p. p. m. (1H, m, H_{5b}). In particular the endo stereochemistry is deduced from the upfield shifts of the H_{5b} and H_{6b} resonances, relative to those of their geminal partners, which results from shielding by the π electron system of the cyclohexa-1,3-diene ring. The adduct reacted readily with dienophiles and tetracyanoethylene for example yielded a compound (210-212° C dec.) whose spectroscopic properties and elemental analysis are consistent with its formulation as the Diels Alder adduct (4).



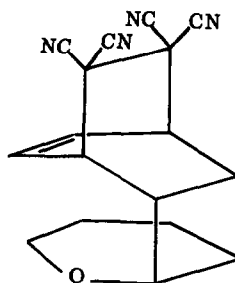
(1)



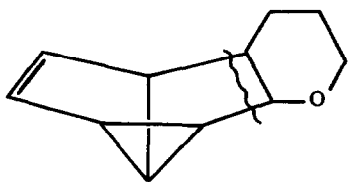
(2)



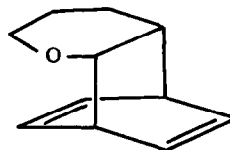
(3)



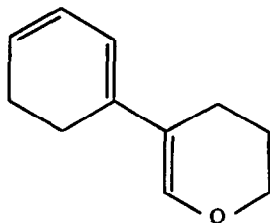
(4)



(5)



(6)



(7)

The minor reaction products are deduced to be the 1,3- and 1,4-cycloadducts (5) and (6) on the basis of their lack of reactivity with dienophiles and u. v., i. r. and n. m. r. spectra of enriched mixtures of the two isomers and their comparison with those of adducts of known structure.^{1, 2}

The 1,2-cycloaddition of 2,3-dihydropyran to benzene is a very efficient process and from 1.1M benzene and 3.5 olefin in iso-octane solution, the quantum yield for this process was determined as 0.7 which is almost twice that of the highest value yet reported for any benzene addition reaction. Under the above conditions the $\Phi_{1,2}$ to $\Phi_{\text{other adducts}}$ ratio was in excess of 15 which demonstrates the high selectivity of the process in comparison with other benzene-donor ethylene systems. The selectivity can be further improved for while the 1,3-cycloaddition process is unaffected by solvent polarity,^{1, 5} the corresponding 1,2-addition reaction is enhanced in solvents of high dielectric constant: in the present case using acetonitrile as diluent, the quantum yield for formation of (3) was 0.76. This result supports the proposal¹ that 1,2-cycloaddition of ethylenes to benzene involves a polar intermediate. No evidence for ground state charge-transfer absorption between the addends was obtained but from n. m. r. chemical shift data of 2,3-dihydropyran in C_6D_6 and CCl_4 solution,⁶ it would appear that benzene and the ethylene form a weakly associated complex in which the molecules have an endo arrangement.

2,3-Dihydropyran quenched the fluorescence of benzene with k_q values of 3.8 to 8.99 x 10⁸ l mol⁻¹ s⁻¹ dependent upon dielectric constant of the solvent. No exciplex emission was observed and the intermediacy of such a species in 1,2-cycloaddition of ethylenes to benzene remains unproven.

In an attempt to determine the excited state of benzene responsible for the formation of (3) we have examined the reaction in the presence of cyclopropyl bromide.⁷ From experiments in which by-product formation was unimportant and absorption of the bromide at 254 nm was taken into account we observe that the rate of formation of (3) is reduced by 60% in the heavy atom solvent and hence the singlet excited state is implicated in the addition process.

The dependence of formation of (3) on reactant concentration and time of irradiation merely results from the photolability of the adduct which undergoes both direct and benzene-sensitised photodecomposition to trace amounts of the starting materials and polymer. In contrast (3) pyrolysed smoothly at 300° C to yield an isomer whose structure is deduced to be (7) from its chemical and spectroscopic properties.

Acknowledgements

The P. C. M. Unit, Harwell, are thanked for 220 MHz n. m. r. spectra and the Science Research Council for a Studentship (G. T.)

References

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3. The magnitude of this coupling constant cannot be used to assign the adduct stereochemistry as its value falls in the overlap region for cis and trans 1,3-coupling of protons on cyclobutane rings.⁴
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6. For similar studies with other olefins see D. Bryce-Smith, A. Gilbert, and H. M. Tyrrell, J. C. S. Chem. Comm., 1974, 699 ; P. Schuler and H. Heusinger, J. Mol. Struct., 1975, 28, 1, 25.
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