

## Photoaddition of Furan to Benzene

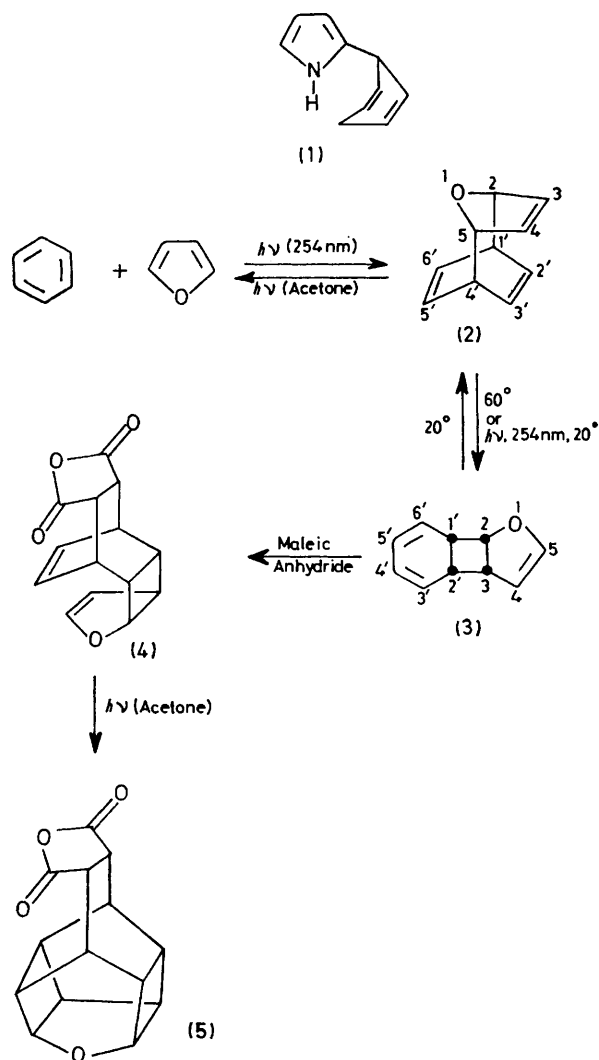
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*Summary* Furan is shown to undergo a novel photochemical 2,5-, 1',4'-cycloaddition to benzene; the product readily undergoes reversible thermal, or irreversible photochemical Cope rearrangement to a 2,3-, 1',2'-isomer.

Of the five-membered aromatic heterocycles, pyrrole undergoes acyclic 1,4-photoaddition to benzene giving (1),<sup>1</sup> and thiophen is substantially photoinert to benzene;<sup>2</sup> in comparison, cyclopentadiene gives mostly dimers,<sup>3</sup> with traces of five non-aromatic 1:1 photoadducts.<sup>2</sup> We now report the photochemical cycloaddition of furan to benzene.

Irradiation (low-pressure mercury arc; 20°; air or N<sub>2</sub>) of an equimolar mixture of benzene and furan gives fulvene together with a mixture of five 1:1 photoadducts (m.s.-g.l.c.,  $\Phi_{\text{total}}$  0.073), and some material of higher molecular weight.



The relative proportions of the adducts were time dependent and from a typical preparative experiment which yielded 0.6 g of the distilled mixture in 60 h from 400 ml solution, the ratio of 1:1 adducts was *ca.* 1:1:6:20:4 (elution on OV 225). The photoadducts were too labile for isolation under the conditions required by various chromatographic procedures, but analytical g.l.c. was feasible. The major component was obtained pure by extraction of the mixture with methanolic silver nitrate and treatment of the crystalline complex with aqueous ammonia. The assignment of a 2,5-1',4'-structure (2) follows clearly from the

n.m.r. spectrum which had resonances at 6.45 (2H, q, H-5', H-6'), 6.10 (2H, q, H-2', H-3'), 6.03 (2H, d, H-3, H-4,  $J_{2,3}$  0.6 Hz), 4.05 (2H, dd, H-2, H-5,  $J_{2,1'}$  6.6 Hz), and 2.95 p.p.m. (2H, m, H-1', H-4'). Spin decoupling experiments substantiated this assignment. The adduct (2) rearranged very cleanly both photochemically and thermally to an isomeric adduct (3) which proved to be identical with the second most abundant component of the original mixture of irradiation products. The *endo* 2,3-1',2'- structure was assigned on the basis of its spectral and chemical properties. N.m.r. resonances occurred at 6.30 (1H, dd, H-5,  $J_{4,5}$  2.8 Hz,  $J_{3,5}$  5.2 Hz), 5.55–5.20 (5H, m, H-3', H-4', H-5', H-6', H-2), 4.95 (1H, t, H-4,  $J_{3,4}$  2.8 Hz), and 3.3–3.9 p.p.m. (3H, m, H-3, H-1', H-2'). The thermal Diels-Alder adducts with maleic anhydride (4) (quantitative yield), *N*-phenylmaleimide, and tetracyanoethylene had m.p.s. 180–183° (decomp.), 188–190° (decomp.), and 218–222° (decomp.) respectively.

Thermal Cope rearrangement of adduct (2) to (3) occurred readily at 60°, ( $t_{1/2}^{60}$  *ca.* 2 h, 0.6M in CCl<sub>4</sub>). The position of equilibrium was remarkably temperature dependent, and partial reversion of (3) to (2) occurred at 20°; but isomer (3) appeared stable below –10°. The rate of thermal isomerisation of (3) into (2) is far too slow to account for the formation of more than a trace of isomer (2) by this route under the preparative conditions. Concerted thermal rearrangement of adduct (2) would be expected to give the *endo* isomer (3), and the thermal Diels-Alder adducts of (3) would have *endo endo* stereochemistry. The assigned structure (4) for the maleic anhydride adduct is based partly upon elemental analysis and mass spectrometric evidence, and the i.r. spectrum which showed structurally significant peaks at 3060 and 2980 (C–H stretch), 1860 and 1781 (C=O in five membered saturated cyclic anhydride), 1382 and 1365 (methine deformation) and 1240 and 1070 cm<sup>-1</sup> (vinyl ether). In particular, the *endo endo* stereochemistry of adduct (4), and thence the *endo* structure of (3) is assigned on the basis of the following spectroscopic and chemical evidence. The n.m.r. spectrum (60 MHz in CDCl<sub>3</sub>) showed resonances at 5.8 (3H, br m, 2 vinyl, 1 furan  $\alpha$ -vinyl), 4.6 (2H, m, furan  $\beta$ -vinyl, furan  $\alpha$  on C<sub>4</sub> ring) with broad multiple resonances between 2.2 and 4.0 including a dominant triplet ( $J$  0.5 Hz) at 2.8 p.p.m. (2H, anhydride). A lanthanide shift experiment [Eu(fod)<sub>3</sub>] established the non-equivalence of the vinyl protons of the benzene residue in adduct (4), thereby indicating *endo* rather than *exo* stereochemistry. The u.v. spectrum of (4) (EtOH;  $\lambda_{\text{max}}$  225 nm,  $\epsilon = 1870 \text{ mol}^{-1} \text{ l cm}^{-1}$ ) indicates substantial electronic interaction between the two ethylenic groups.<sup>4</sup> Final confirmation was provided by acetone-photosensitised intramolecular cyclisation to the cage isomer (5), the n.m.r. spectrum of which showed the absence of vinyl protons.

Isomer (2) yields no detectable amounts of (3) after standing for 7 days at 20° but is almost completely converted into (3) within a few minutes at 20° on irradiation of solutions in CCl<sub>4</sub> at 254 nm. The survival of major proportions of (2) under the preparative conditions results from the screening effect of benzene. Similar irradiation of (3) gave no detectable amounts of (2); traces of benzene and furan were also formed in each case. Under conditions of triplet photosensitisation (acetone or benzene), isomers (2) and (3) showed no interconversions, but each dissociated to give furan. These findings, in conjunction with the observation that the ratio of (3) to (2) tends to increase with

time in the irradiation of mixtures of benzene and furan, indicate that isomer (2) is a primary photochemical product. Since (2) and (3) are both present in the product mixture even after the shortest feasible irradiation times (*ca.* 2 h) it cannot yet be decided whether all of (3) arises by isomerisation of (2).

The three minor 1:1 adducts have not yet been definitely characterised, but preliminary studies suggest that they are

probably 1,3-cycloadducts of the type formed from simple olefins and benzene.<sup>5</sup>

The formation of adduct (2) from benzene and furan provides the first example of the cycloaddition of two monocyclic aromatic systems.

(Received, 16th September 1974; Com. 1170.)

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<sup>2</sup> J. C. Berridge and A. Gilbert, unpublished work.

<sup>3</sup> K. Kraft, Ph.D. Thesis, University of Bonn, 1968.

<sup>4</sup> C. F. Wilcox, S. Winstein, and W. G. MacMillan, *J. Amer. Chem. Soc.*, 1960, **82**, 5450.

<sup>5</sup> K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 2066; D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1966, 512.