Tetrahedron Letters No. 45, pp 3959 - 3962, 1974. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL ADDITION OF BENZENES TO FURAN

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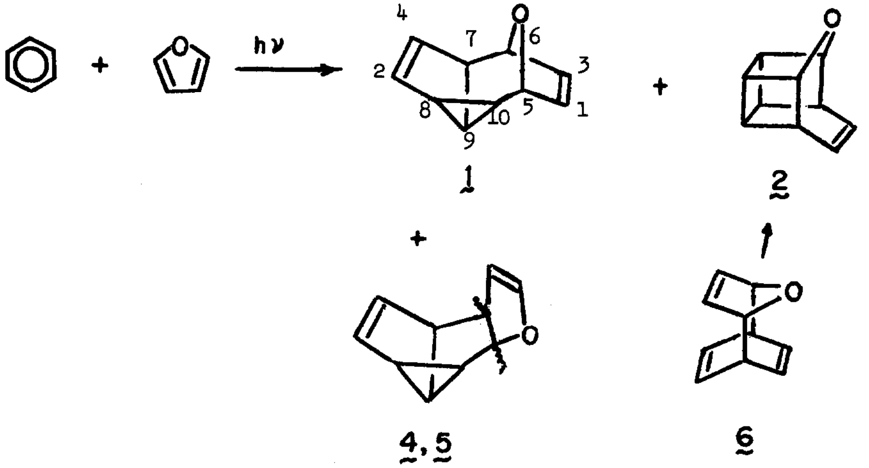
(Received in USA 9 July 1974; received in UK for publication 3 October 1974)

Photochemically excited benzene and its simple alkyl derivatives undergo cycloaddition to olefins predominantly in a 1,3 manner, with smaller amounts of products resulting from 1,2 and 1,4 addition across the benzene ring sometimes being observed.[1-5] Photochemical addition of benzene to butadiene and 2,3-dimethylbutadiene gave complex mixtures of products; the major products identified were those resulting from 1,3 - 1,2[5] and 4 + 4 cycloaddition.[5,6] We report here the photochemical cycloaddition of benzene and methylated benzenes to furan and cyclopentadiene, which give predominantly adducts resulting from a novel 1,3 - 1,4 addition process.

Irradiation of benzene-furan mixtures at 2537 A^{o} (or with a Hanovia 450-watt source and Vycor filter) for 4 hours gave, after evaporation of excess reactants, ~ 0.5 g of a yellow residue. Distillation of the combined residues from three such runs gave 1.1 g of colorless oil, bp 47-49^{o}/0.08 mm. Separation by gc on SE-30 at 180^{o} gave adducts 1-5 in a ratio of 58:23:11:5:4. The structure of the major adduct, 1 [m/e 146 (P,8), 145 (10), 117 (47), 115 (38), and 81 (100)] was deduced mainly from its nmr spectral parameters (Table I), obtained via extensive decoupling experiments and by comparison with the spectrum of the adduct from benzene-d_6 and furan. The stereochemistry was assigned as shown on the basis of lanthanide-induced shifts (LIS) observed for 1 and 1-d_6 on addition of Eu(fod)$_3$. Thus, H_2 and H_4 exhibit greater LIS's than do H_9 and H_{10}. Since the oxygen atom must be the site of coordination to the europium, the observed LIS's demand that H_2 and H_4 be syn to the oxygen bridge.

The structures of 2 [ir (film): 1070 cm^{-1}; nmr: τ 3.84 (2H, 2d, J = 4.8, 3.0), 5.3 - 5.5 (2H, m, br), 6.4 - 6.8 (4H, m, br), and 7.2 - 7.5 (2H, m); m/e 146 (P,11), 145 (14), 117 (60), 115 (53), 91 (35), 78 (57), and 68 (100)] follows from its spectral characteristics, in particular, the simplicity of its nmr spectrum. Compound 2 evidently is an artifact arising from benzene-sensitized intramolecular 2 + 2 cycloaddition of the presumed intermediate 6, a 4 + 4 cycloadduct of



NMR DATA FOR 1

	H_1	H_2	H_3	H_4	H_5	H_6	H_7	H_8	H_9	H_{10}
τ	3.60	3.85	3.96	4.63	4.95	5.64	7.00	7.83	8.41	9.30
LIS[a]	1.57	3.20	1.78	3.55	5.5	7.7	3.18	2.12	2.74	2.38

$J_{7,9} = 7.4$ $J_{6,7} = 2.1$ $J_{1,3} = 6.2$

$J_{2,8} = 2.5$ $J_{3,6} = 1.8$ $J_{2,4} = 5.8$

$J_{8,9} = 7.5$ $J_{1,5} = 1.9$ $J_{3,6} = 1.8$

$J_{9,10} = 7.5$ $J_{5,10} = 1.5$ $J_{2,7} = 2.1$

[a] 0.3 equiv of Eu(fod)$_3$ added.

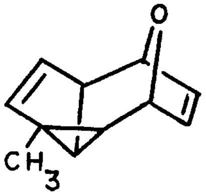
TABLE I

benzene and furan.

Products 4 [ir (film): 1605 cm^{-1}; nmr: τ 3.58 (1H, t, J = 1.4), 4.46 (2H, m), 5.18 (1H, m), 5.26 (1H, d, J = 7), 6.67 (1H, d of m, J ~ 7), 6.82 (1H, d of m, J ~ 7), 7.51 (1H, d of d of d, J = 7.8, J' = 7), and 8.12 (2H, d, J = 7.8); m/e 146 (P, 32), 117 (95), 115 (90), 81 (100), and 68 (48)] and 5 [ir (film): 1600 cm^{-1}; nmr: τ 3.82 (1H, 2d, J = 2.8, J' = 1.9), 4.68 (1H, d, J = 9), 5.40 (1H, 5, J = 2.8), 6.35 (1H, d, br, J = 9), 7.1 (1H, 2d, J = 9, J' = 2), 7.8 (1H, q, J = 9), and 8.2 (2H, m); m/e 146 (47, P), 117 (75), and 81 (100)] were assigned the structures shown on the basis of the similarities of their nmr spectra and those of known 2,3-dihydrofurans[7] and known

1,3-photoadducts of benzene with simple olefins.[3,4] Compound 3, whose structure has not been completely elucidated, is apparently a secondary photoproduct, like 2. The photochemical reaction of benzene with furan is an efficient process, as shown by the respective quantum yields for 1 and 2 of 0.27 and 0.11[8] (compared with 0.17 for addition to cyclopentene under similar conditions[4]).

Toluene and xylene when irradiated with furan give product mixtures in which ethylated analogs of 1 and 2 predominate; for example, the major products from toluene are 7,8, and 9 in the ration:30:50:20 Details on these and related compounds will be given in the full publication.



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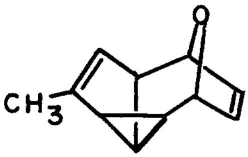

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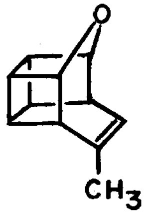

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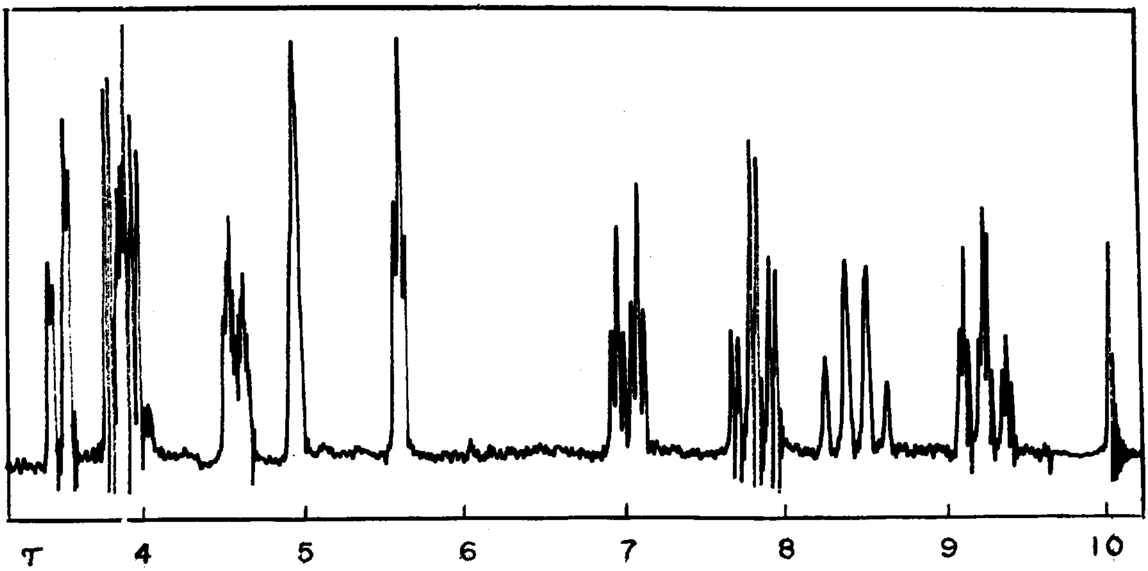
Irradiation of the 3:1 mixtures of benzene and 2,5-dimethylfuran led to complex mixtures of ketones similar to those obtained on direct irradiation of the dimethylfuran.[9] It would appear that energy transfer from excited benzene to the dimethylfuran is occurring.

Yang[5] and others[6] have reported that among the major products from photochemical addition of benzene to acyclic 1,3-dienes are those resulting from 4 + 4 cycloaddition. We have observed the 1,3-1,4 process which leads to 1, to be the major process in the case of xylene and cyclopentadiene. Irradiation of a 5:1 mixture of these substances gave 10, a 7,8-dimethyl derivative of 1 (55%), 11, a dimethyl derivative of 4 or 5 (30%) and a minor product (15%) of unknown structure. The nature of 10 and 11 was evident from the appearance of their nmr spectra. The assignment of 10 as a product resulting from 1,4,rather than 1,2 addition to cyclopentadiene, is based on the appearance of nmr signals assignable to the bridge methylene hydrogens at τ 8.3 and 8.6. Typical norbornenes show bridge methylene signals in this region,[10] whereas 2 + 2 adducts to cyclopentadienes, such as 11, show signals for allylic methylene hydrogens at τ 7,0 - 7.6.

ACKNOWLEDGEMENTS

The author is deeply grateful to Dr. Herman Yeh of the National Institutes of Health for the decoupling experiments.



NMR Spectrum of 1

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