# Photoaddition of Furan to Benzene: Sensitivity to Reaction Conditions

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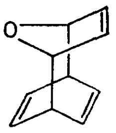
*Summary* Evidence is presented which largely, though not entirely, reconciles two recent seemingly discrepant reports on the photoaddition of furan to benzene.

We have recently described the photoaddition of furan to benzene in two seemingly conflicting independent reports.[1,2] The conclusions from our consultations and further experiments have largely clarified this matter. It now transpires that most of the apparent discrepancies arose from the differing experimental conditions used in the two studies.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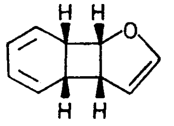

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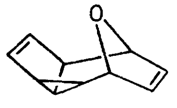

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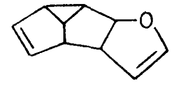

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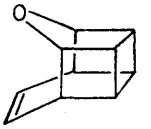

(5)

Irradiation of 1 : 1 v/v benzene–furan mixtures (20°, air or $N_2$) with a low-intensity low-pressure mercury arc (rated 6 W at 254 nm) yields the 1 : 1 adduct (**1**) as the major product as previously reported.[1] This adduct and its Cope-rearranged isomer (**2**), which is also formed in the irradiation, are best isolated as the adducts with silver nitrate and maleic anhydride respectively.[1]

Adducts (**1**) and (**2**) dissociate to the starting materials at the temperatures which are necessary to separate the components of the reaction mixture by preparative g.c., so this technique only affords the more thermally stable minor components, *viz.* the 1,3–2′,5′-adduct (**3**), the 1,3–2′,3′-adduct (**4**), and the 'cage' isomer (**5**) formed by photocyclisation of adduct (**1**).[2] This is one of the reasons why (**1**) and (**2**) were not detected in one of the earlier studies.[2]

Adducts (**1**) and (**2**) both absorb significantly at 254 nm and are photolabile when irradiated with light of this wavelength; adduct (**1**) efficiently yields (**2**) and very minor amounts of (**5**), but both (**1**) and (**2**) also undergo slow photolysis to the starting materials. This dissociation process is photosensitised by benzene or acetone.[1] In contrast, the other adducts (**3**), (**4**), and (**5**) of furan and benzene[2] absorb only relatively weakly at 254 nm and are essentially photostable in the absence and presence of benzene. The observation[1] of adducts (**1**) and (**2**) as major products has been confirmed in both laboratories and may be attributed to the use of a low-intensity and substantially monochromatic source, and the screening effect of the high concentrations of benzene. On the other hand, we find that irradiation of furan–benzene mixtures with a high intensity medium-pressure source (Hanovia 450 W mercury lamp and a Vycor filter transmitting at wavelength > 240 nm) at comparatively low benzene concentrations[2] favours the continual build-up of adducts (**3**), (**4**), and (**5**) and destruction of adduct (**1**) and its isomer (**2**).

Thus it is now evident that the two earlier reports can be substantially reconciled by the observations that the proportions of the various adducts from furan and benzene are dependent upon the light source and reactant concentrations. It is also important for the isolation of adducts (**1**) and (**2**) that temperatures as near to ambient as possible should be used in the work-up procedures.

We do, however, remain irreconciled on the quantum yield aspects. One of us (T.S.C.) has confirmed the previously reported[2] quantum yield of 0·27 for formation of adduct (**3**) at 254 nm in cyclohexane. Although we all agree that adduct (**1**) is a major product, the Reading authors have repeatedly obtained a value of 0·075 ± 0·005 for the quantum yield of formation of the total 1 : 1 adducts in cyclohexane, of which 0·045 corresponds to the primary adduct (**1**). It is hoped that further studies will clarify this residual discrepancy.

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[1] J. C. Berridge, D. Bryce-Smith, and A. Gilbert, *J.C.S. Chem. Comm.*, 1974, 965.
[2] T. S. Cantrell, *Tetrahedron Letters*, 9174, 3959.