

1,4-Photoaddition of Diethyl Ether to Benzene

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Summary Benzene undergoes a novel acid-catalysed 1,4-photoaddition of diethyl ether, giving adduct (I),

THE recently reported acid-catalysed photoreactions of benzene with certain acceptor molecules such as *p*-benzoquinone and maleic anhydride appear to involve protonation of a zwitterion formed following electron-transfer from benzene to the acceptor; they may be classified as photo-electrophilic aromatic substitutions.¹ We now report an acid-catalysed photoreaction of benzene which apparently involves electron-transfer in the reverse sense, and leads to 1,4-addition rather than substitution.

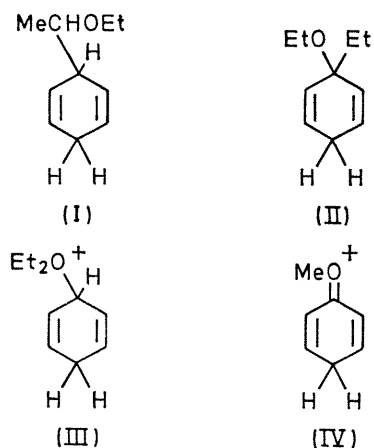
Irradiation of an equimolecular mixture of benzene and diethyl ether (15°; 254 nm) in the presence of 0.3 mol. equiv.

of trifluoroacetic acid leads to the 1:1 adduct (I) as essentially the only product: τ (100 MHz) 9.0 (d, 3H, *J* 6 Hz, MeCH), 8.86 (t, 3H, *J* 7 Hz, MeCH₂), 7.36 (d, 2H, *J* 8 Hz, ring CH₂), 7.10 (m, 1H, ring CH), 6.75 (q, 1H, *J* 6 Hz, CHMe), 6.60 and 6.58 (2 q, 2H, *J* 7 Hz, MeCH₂), and 4.15—4.6 (m, 4H, CH=C); ν_{\max} (significant absorptions) 3000 (vinyl C-H), 1640 (C=C), and 1135 cm⁻¹ (C-O); *m/e* 152, 150, 135, 107, 105, 91, 83, 79, and 73 (base peak): *M* - 2 = 150.1044 (C₁₀H₁₄O requires 150.1045). The fragmentation pattern is consistent with initial loss of 2H to form the aromatic ion corresponding to (I). These properties rule out the alternative structure (II).

Hydrogen chloride could be used in place of trifluoroacetic acid, but no trace of adduct (I) was found in the

absence of acid. The given 0.3 mol. proportion of acid appears to be approximately optimal. Above 1.0 mol. proportion, the yield of adduct (I) is greatly reduced and $\text{PhCO}\cdot\text{CF}_3$ and other products of a photoreaction between benzene and trifluoroacetic acid begin to appear,² but these are not formed to any appreciable extent when the ether is in molar excess over the acid. No comparable reaction occurred with di-isopropyl ether in place of diethyl ether, and benzonitrile or anisole in place of benzene.

Mixtures of benzene and diethyl ether show no charge-transfer absorption, and addition of diethyl ether to mixtures of benzene and trifluoroacetic acid† causes no



optical changes other than dilution effects. Any electron-transfer involving the ether must therefore occur after the electronic excitation. Since (a) the protolytic equilibria involve both the ether and the benzene, (b) a molar excess of ether over acid appears to be necessary, (c) methanol (which readily protonates the benzene radical-anion) cannot be used in place of trifluoroacetic acid, and (d) none of the by-products expected for a free radical process could be detected, it appears likely that electron-transfer from unprotonated ether to an excited C_6H_7^+ species, leading to the intermediate (III), is mechanistically important. The subsequent deprotonation-rearrangement of cation (III) to adduct (I) would provide an oxonium analogue of the Stevens rearrangement. Although there are some grounds for expecting that such a rearrangement might give the alternative product (II), no trace of this could be found.

This mechanism is consistent with the observed unreactivity of benzonitrile, but not, at first sight, with the failure of anisole to undergo addition. However, since anisole is itself an ether, its apparent unreactivity could result from a dominance of intramolecular electron-transfer, *i.e.* structure (IV) may be an important contributor to the S_1 state of protonated anisole.

The present process bears a certain similarity to the 1,4-photoaddition of amines to benzene,^{3,4} and to the Birch reduction, but differs from these in (a) the absence of radical coupling products such as tetrahydrobiphenyl, and (b) its insensitivity to methanol as a proton-donor.⁴

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† Differential thin-film spectra of such mixtures show λ_{max} 217 nm, an absorption which we suggest may be attributed to the benzenonium ion since it also appears in the corresponding spectra of solutions of sulphuric and methanesulphonic acids in benzene.

¹ D. Bryce-Smith, R. Deshpande, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 561.

² D. Bryce-Smith, G. B. Cox, and A. Gilbert, preceding communication.

³ M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 263, 862.

⁴ D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, following communication.