1,4-Photoaddition of Aliphatic Tertiary Amines to Benzene: Effect of Proton Donors

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Summary Tertiary amines undergo 1,4-photoaddition to benzene; the reaction is greatly accelerated in the presence of a proton-donor such as water or methanol.

THE 1,4-photoaddition of primary and secondary amines, including pyrrole, to benzene has previously been described.[1] We now report that aliphatic tertiary amines also undergo 1,4-photoaddition to benzene, especially in the presence of a proton donor.

Irradiation (medium-pressure mercury arc lamp; 20° N_2) of an equimolar mixture of triethylamine and benzene leads to small amounts of the adduct (I) and traces of the tetrahydrobiphenyl (II) and cyclohexa-1,4-diene, but the main products were the same as those formed from irradiation of triethylamine in the absence of benzene.[2] Identification of adduct (I) rests on mass spectrometric, n.m.r., and i.r. data. It was dehydrogenated by *p*-chloranil in refluxing xylene to the aromatic derivative (III), the identity of which was confirmed by a conventional alternative synthesis (picrate m.p. 131°, lit.,[3] 131°).

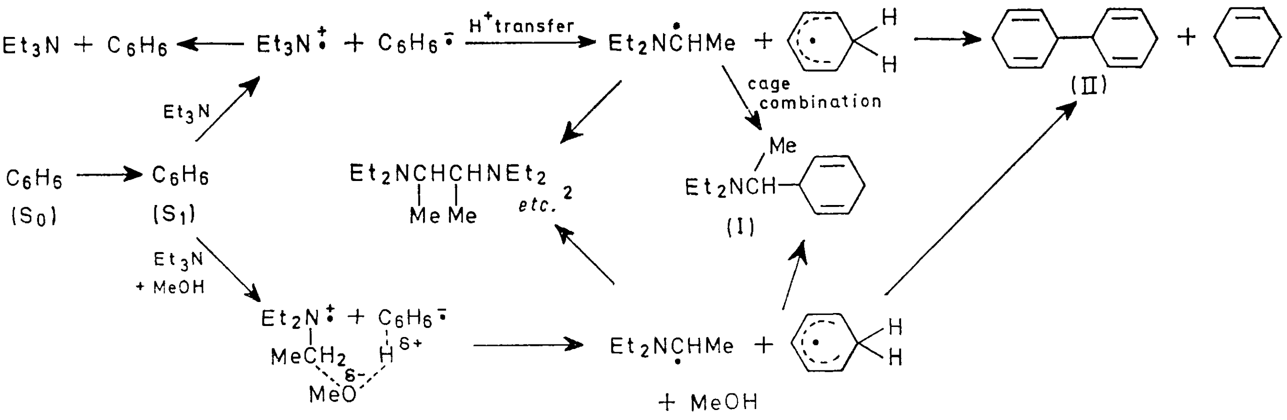
An adduct analogous to (I) has been obtained by Barltrop and Owers as a minor product of the photoreaction between naphthalene and triethylamine.[4] Cookson *et al.* have reported that triethylamine photo-adds to the ethylenic bond in styrene.[5]

Suspecting the involvement of a proton-transfer step in addition of the tertiary-amine to benzene, we repeated the reaction in the presence of 10 mol. % of methanol. The rates of formation of the 1,4-adduct (I), the tetrahydrobiphenyl (II), and cyclohexa-1,4-diene were all increased approximately eightfold, and adduct (I) now constituted 80% of the total reaction products, with *ca.* 2% each of the other two components. Similar results were obtained by the use of water and trimethylammonium trifluoroacetate as proton donors. The materials used for the reactions performed in the absence of added proton donors were carefully purified and dried, so it appears that free or complexed triethylamine can act as a feeble proton donor.[†] Acetonitrile did not promote the formation of adduct (I), so the effects of methanol *etc.* cannot be attributed to solvent polarity alone.

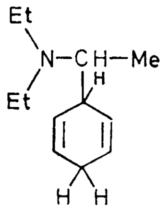
Similar effects of proton donors have been found for the corresponding 1,4-photoadditions of trimethylamine and tri-n-butylamine to benzene. Methanol shows a smaller promoting effect on the corresponding 1,4-addition of diethylamine, giving adduct (IV), and only a slight effect on the addition of cyclohexylamine (*cf.* ref. 1). Evidently the primary and secondary amines themselves function as proton donors. The methanol-promoted photoadditions of Me_2NEt and $MeNEt_2$ to benzene lead in each case to reaction at both the methyl and methylene groups with products from the former predominating in the ratios 6:1 and 2:1 respectively (n.m.r. and mass spectra).

The present results indicate the importance of proton-transfer in 1,4-photoadditions of amines to benzene, and may usefully be compared with the 1,4-photoaddition of diethyl ether to benzene.[6] Addition of the ether requires strong acid such as trifluoroacetic acid, but methanol is without effect. Methanol can protonate the benzene radical anion (as in the Birch reduction) but not benzene itself, whereas trifluoroacetic acid can protonate both. Thus the effects of acid strength provide a strong indication that proton-transfer essentially occurs subsequently to electronic excitation in the addition of amines to benzene and prior to excitation in the corresponding addition of diethyl ether.

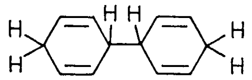
The 1,4-addition of amines to benzene appears to be a non-concerted process and to involve both inter- and intramolecular proton-transfer steps. Thus, thermal 1,4-dehydrogenation (300°) of the adducts of triethylamine and trimethylamine with hexadeuteriobenzene, a known *cis*-elimination, leads to the loss of H_2 and HD in equal proportions. The pyrrole–hexadeuteriobenzene adducts, however, lost HD and D_2 in the ratio 2:3 thereby establishing a slight predominance of the *cis*-isomer (V) which would result from a contribution from intramolecular hydrogen-transfer within a zwitterionic intermediate (VI).



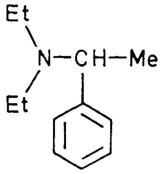
SCHEME



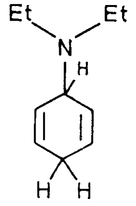
(I)



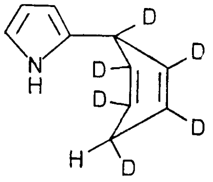
(II)



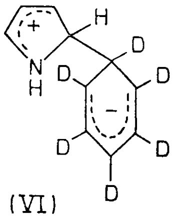
(III)



(IV)



(V)



(VI)

Oxygen does not totally inhibit the formation of adduct (I), and unlike nitrogen, permits the formation on irradiation at wavelengths > 300 nm, together with much tarry material (which soon acts as an internal light filter). Oxygen-free mixtures of triethylamine and benzene show u.v. absorption which is substantially additive of that of the components, but brief exposure of such mixtures to air leads to the appearance of a marked new absorption, λ_{max} 290 nm, which disappears on de-gassing. We are investigating the possibility that this corresponds to the normally

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[†] The notorious ubiquity of water discourages us from undue emphasis on this point.

strongly forbidden $S_0 \rightarrow T_1$ transition in benzene. Concentration studies have indicated that the chemical yield of adduct (I) in the absence of oxygen depends directly on the proportion of radiation absorbed by the benzene rather than the triethylamine.

The Scheme is therefore proposed for the reactions which occur in the absence of oxygen. This Scheme is further supported by the observation that D from MeOD is incorporated at the 4-position of adduct (I).

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[2] L. T. Allan and G. A. Swan, *J. Chem. Soc.*, 1965, 4822.
[3] G. A. Swan, P. S. Timmons, and D. Wright, *J. Chem. Soc.*, 1959, 9.
[4] J. A. Barltrop and R. J. Owers, *Chem. Comm.*, 1970, 1462.
[5] R. C. Cookson, S. M. de B. Costa, and J. Hudec, *Chem. Comm.*, 1969, 753.
[6] D. Bryce-Smith and G. B. Cox, preceding communication.