# 1,4-Photoaddition of Amines to Benzene

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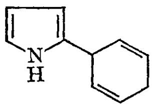
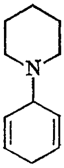
IN a recent Communication[1] we described the formation of 2-(cyclohexa-2,5-dienyl)pyrrole (I) by the 1,4-photoaddition of pyrrole to benzene. We now report that simple primary and secondary aliphatic amines also readily undergo 1,4-photoaddition to benzene; but the major products in these cases contain the cyclohexadienyl group linked directly to nitrogen.

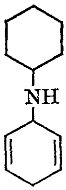
Irradiation of piperidine in an excess of benzene under nitrogen at 20° (medium-pressure mercury vapour lamp) gave a colourless oil, b.p. 90°/0·2 mm. Over 95% of this was a single component which was isolated and shown by elemental analysis and mass spectrometry to be a 1 : 1-adduct. This is assigned structure (II) on the basis of the following chemical and spectroscopic evidence.



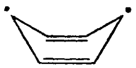
(I)



(II)



(III)



(IV)

The compound is soluble in dilute aqueous mineral acids, and is reprecipitated unchanged by alkali. Hydrogenation of its unstable hydrochloride (10% Pd on C: ethanol) gave benzene and the hydrochlorides of piperidine and *N*-cyclohexylpiperidine. This same unstable hydrochloride failed to react with maleic anhydride or phenyl azide. Treatment of the free base (II) with potassium t-butoxide gave only piperidine and benzene: a similar reversion to the starting materials slowly occurs when the adduct (II) is kept at room temperature.

The ultraviolet spectrum of the adduct (II) in hexane shows $\lambda_{max}$ 213 m$\mu$ ($\epsilon$ 3000) and 254 m$\mu$ ($\epsilon$ 2200). Structurally significant infrared absorptions are sited at 3000 (=C–H), 2900, 2820, 2760 (CH and $CH_2$), 1680 (*cis*–C=C–) and 700 cm.$^{-1}$ (*cis*–H–C=C–H). The n.m.r. spectrum (60 Mc./sec. in $C_6D_6$) clearly identified the cyclohexa-2,5-dienyl group by the presence of peaks at, or centred at, $\tau$ 4·2 (singlet, four vinyl protons), 6·3 (triplet, methine proton), 7·5 (multiplet, two methylene protons in the cyclohexadiene ring, four methylene protons adjacent to nitrogen in the piperidine ring), and 8·5 (multiplet, six methylene protons). Spin decoupling experiments established the existence of characteristic long-range coupling between methine and methylene protons on the cyclohexadiene ring ($J$ = 8 c./sec.), *cf.*, refs. 1 and 2. Resonance attributable to N–H protons was absent.

Irradiation of an oxygen-free solution of cyclohexylamine in excess of benzene at 20° under nitrogen (15 w low-pressure mercury vapour lamp) gave a pale yellow oil (b.p. 60—62°/0·1 mm.) which contained four basic compounds in the approximate ratio 1 : 1 : 5 : 1. The major component was isolated in *ca.* 90% purity *via* fractional crystallisation of the mixed hydrochlorides. Catalytic hydrogenation of its hydrochloride gave benzene, cyclohexylamine hydrochloride, and dicyclohexylamine hydrochloride. Elemental analysis, mass, i.r., u.v., and n.m.r. spectra of the major component and its hydrochloride are consistent with its formulation as a 1 : 1-adduct of structure (III). Work is in progress to elucidate the structures of the other three products.

Methylamine, n-butylamine, and s-butylamine have also been examined as the amine components in this reaction. All have given products seemingly analogous to those formed from cyclohexylamine. Even ammonia and benzene have given small quantities of a 1 : 1-photoadduct. The amounts so far obtained have been inadequate for a definite structural assignment, but we suspect that the product is a dihydroaniline analogous to the adducts described above. Naphthalene also readily forms 1 : 1-photoadducts with primary and secondary aliphatic amines.

From a mechanistic viewpoint, these new reactions, as also that with pyrrole,[1] appear to be satisfactorily accounted for in terms of the intermediate diradical (IV) previously suggested as a possible tautomer of triplet benzene.[3] An alternative mechanism involving free-radical attack on ground-state benzene by $R_2N\cdot$ or $R\underset{\bullet}{N}H$ appears to be excluded by the absence from the photoproducts of any detectable traces (g.l.c.) of the corresponding aminobenzenes.

The recently demonstrated[4] complexing between benzene and amines seems likely to be an important factor in these processes.

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[1] M. Bellas, D. Bryce-Smith, and A. Gilbert, *Chem. Comm.*, 1967, 263.

[2] L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Comm.*, 1965, 456.

[3] D. Bryce-Smith and H. C. Longuet-Higgins, *Chem. Comm.*, 1966, 593.

[4] H. Kehiaian, Abstracts of Chemical Society Anniversary Meeting, Exeter, 3–6 April, 1967, C12.