1,4-Photoaddition of Pyrrole to Benzene

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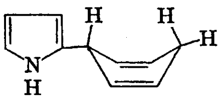
THE protean photochemical character of benzene has in recent years been exemplified by the isomerisation to fulvene and by various 1,2- and 1,3-addition reactions leading to derivatives of bicyclo[2,2,0]hexane and bicyclo[3,1,0]hexene respectively.[1] We report now a 1,4-photoaddition of pyrrole to benzene.

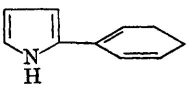
Ultraviolet irradiation of solutions of pyrrole in an excess of benzene at 25° under nitrogen gives a mixture of 1 : 1 adducts of which *ca.* 95% comprises a colourless compound, m.p. 15° [*M* 145·0890 (mass spectrometer); calc., 145·0891].[2] This is assigned structure (I) on the basis of the following chemical and spectroscopic evidence.

The compound is chromatographically homogeneous, and is essentially nonbasic, being virtually unaffected by dilute mineral acids. Catalytic hydrogenation (10% Pd on C) leads to the absorption of 2·0 mol. of hydrogen and the formation of 2-cyclohexylpyrrole plus a trace of 2-phenylpyrrole. Treatment with the catalyst in the absence of hydrogen, or with tetracyanoethylene, gave 2-phenylpyrrole in high yield: similar dehydrogenations of cyclohexa-1,4-dienes are known.[3] The adduct (I) did not add maleic anhydride; but potassium t-butoxide catalysed a prototropic rearrangement to a rather unstable diene which is assumed to have structure (II) since it gave with maleic anhydride a 1 : 1 adduct, m.p. 178° (decomp.), having infrared and n.m.r. spectroscopic properties consistent with structure (III).

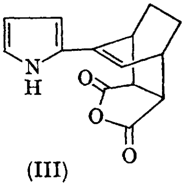
The ultraviolet spectrum of the adduct (I) shows λ_{max} 219 mμ (ϵ 7500) and 275 mμ (ϵ 1100). Structurally significant infrared absorptions are as follows: 3380 (NH), 3100 (pyrrole CH), 2860, and 2820 (CH and CH_2), 1640 (*cis*-C=C), 1560 (pyrrole C–C), and 715 cm.$^{-1}$ (*cis*-HC=CH). The n.m.r. spectrum (60 Mc./sec. in $CDCl_3$) shows a broadened singlet at τ 2·1 (N–H), multiplets between τ 3·3 and 4·2 (three pyrrole protons), a singlet at τ 4·3 (four vinyl protons), a triplet (J = 7 c./sec.) at τ 6·0 (methine proton), and a doublet (J = 7 c./sec.) at τ 7·3 (two methylene protons). Spin-decoupling experiments established that the methine and methylene multiplets arise from long-range coupling between the protons in these groups. This type of transannular coupling has been reported previously for 1-phenylcyclohexa-2,5-diene where the



(I)

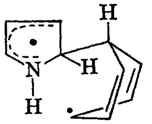


(II)



(III)

(IV)



(V)

corresponding coupling constant is about 9 c./sec.[4]

The rate of formation of adduct (I) decreases with increase in the molecular ratio of pyrrole to benzene, so direct photoexcitation of pyrrole seems unlikely to be involved. Pyrrole and benzene form a weak 1 : 1 complex,[5] but as this shows no charge-transfer ultraviolet absorption beyond the benzene solvent front, the first step in the photoexcitation process is probably a $^1A_{1g} \rightarrow {}^1B_{2u}$ transition in free or complexed benzene.

Formation of adduct (I) accords with a recent suggestion that the triplet diradical (IV) is one of several isomeric intermediates which can arise following photoexcitation of benzene.[1a] α-Addition of such a diradical to pyrrole (*cf.* refs. 6 and 7) would give an intermediate (V) the geometry of which would be favourable for an α,4- or *N*,4-hydrogen shift: the latter possibility is consistent with the failure of *N*-methylpyrrole to form the *N*-methyl derivative of adduct (I) on irradiation with benzene.

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