

Photochemical 1,3-Cycloaddition of Olefins to Aromatic Compounds

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THE formation of 1:1, mono-olefinic, non-aromatic adducts between olefins and benzene has been previously reported by one of us¹ and is part of the subject matter of a British Patent Application (September 1965).

The previously known photochemical cyclic additions to benzenoid rings involve either 1,2-² or 1,4-attack³ of the addend. Chemical and physical evidence reported below indicates formation of the present adducts to arise in a formal sense by 1,3-addition of the olefin to the aromatic ring. Wilzbach and Kaplan have recently reported similar 1,3-cycloadditions of certain olefins to benzene.⁴ This type of addition differs from those previously known in which the ethylenic bond of an addend forms part of a conjugated system as in, for example, maleic anhydride.

In the present systems benzophenone and acetone are ineffective as photosensitisers, but the rates of addition are increased approximately twofold in the presence of β -propiolactone.

The case of cyclo-octene as addend has so far been investigated in the greatest detail. Irradiation at room temperature or in the solid phase at -60° of an equimolar mixture of benzene and *cis*-cyclo-octene with ultraviolet radiation of wavelength 235–285 $m\mu$ leads to a mixture of 1:1 adducts from which the main component (*ca.* 85%) is readily obtained pure by treatment of the mixture with methanolic mercuric acetate. This 1:1 adduct (a colourless liquid b.p. $80-82^\circ/0.2$ mm.) is assigned structure (I) on the basis of the following chemical and physical evidence.

The molecular weight (mass-spectrometric) and elemental analysis are consistent with a 1:1

adduct of benzene and cyclo-octene. The compound responded to the usual tests for unsaturation, and peroxy-acid titration indicated the presence of one ethylenic bond. Catalytic hydrogenation with 10% palladium on carbon in ethanol led to the rapid uptake of 1 mol. of hydrogen followed by the slower uptake of a further 1 mol. Only 1 mol. of hydrogen was readily taken up in benzene. There was no reaction with dimethyl acetylenedicarboxylate under the usual conditions for Diels-Alder addition, but crystalline 1:1 adducts, evidently (II), m.p. 214° , and (III), m.p. 167.5° (with loss of nitrogen), were formed with tetracyanoethylene and phenyl azide respectively. The adduct (I) has good thermal stability, but slowly decomposed to resinous material when heated above 200° under nitrogen: it is significant that no benzene was formed.

The ultraviolet spectrum shows λ_{\max} 219 $m\mu$ (ϵ , 2800): these figures are similar to those reported for similar structures.⁵ Structurally significant peaks in the infrared spectrum are as follows: 3040, 3020, 3010, 2940, 2910, 2890, and 2850 cm.^{-1} (C-H stretch), 1600 cm.^{-1} (strained C=C), and 1465, 1445, and 1355 cm.^{-1} (methine and methylene deformation), 720 cm.^{-1} [$-\text{[CH}_2\text{]}_6-$?] and 679 cm.^{-1} (*cis*-ethylene). The n.m.r. spectrum (60 Mc./sec. in CCl_4) shows signals centred at τ 4.5, (integral 2) and τ 7–9.2 (integral 18). The splitting patterns in the regions τ 4.3–4.7, 7–7.3, and 7.3–7.8 are identical with those reported for tricyclo[3,3,0,0²,⁸]oct-3-ene.⁵

The minor non-aromatic adduct (10–15% of the total isomeric products) undergoes ready thermal isomerisation and has not yet been obtained wholly

Preliminary work suggests that 1:1 adducts analogous to compound (I) are formed by 1,3-

photoaddition of unconjugated acetylenes, for example hex-3-yne, to benzene.

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¹ Paper read by A. Gilbert, Autumn Meeting of the Chemical Society at Nottingham, October 1965.

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