A New Photochemical Reaction of the Benzene Ring

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EXCITATION of benzene with light at 254 mμ in the liquid phase, in the presence of dissolved mono-olefins, results in 1,3-addition to the ring.[1] In the presence of chloro-olefins a new reaction occurs, revealed by the appearance of u.v. absorption bands which can be assigned to chlorine-substituted, linear tetraenes, whose absorption maxima are presented in the Figure.

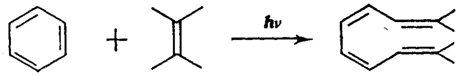
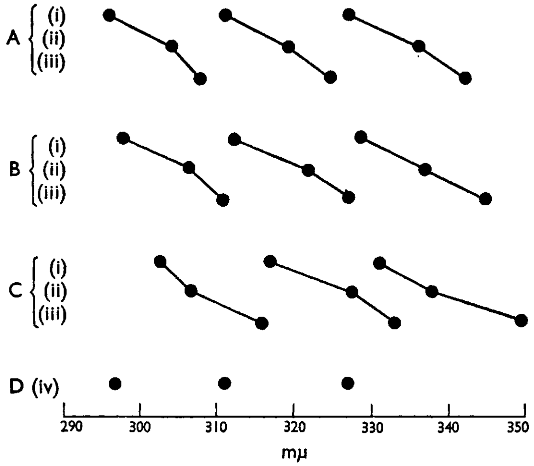


FIGURE. *Absorption maxima of substituted olefin adducts in isopentane–methylcyclohexane solutions at* 90° K.
A, Benzene; B, Toluene; C, Anisole; D, Benzonitrile. (i) $C_2H_2Cl_2$ (all isomers), (ii) C_2HCl_3, (iii) C_2Cl_4, (iv) C_2HMe_3.

Substitution of a chlorine atom in the 1 or 2 positions of hexatriene produces a bathochromic shift of 8 mμ and zero, respectively.[2] Assuming the same behaviour in octatetraene, the maxima lie at wavelengths consistent with substitution only on the terminal atoms (see Table); the overall reaction can be written as



An analogous reaction occurs with benzonitrile and trimethylethylene: the bicyclic adduct isolated after many days irradiation by Atkinson *et al.*,[3] was not detected. Assuming the tetraene absorption has a maximum extinction ~5 × 10^4 M^{-1} $cm.^{-1}$, and a linear dependence on light intensity, it is produced with a quantum yield ~10^{-2}.

The reaction proceeds in the liquid phase, in dilute solution (~10^{-2} – 10^{-3} M) in hexane at room temperature, more rapidly in isopentane–methylcyclohexane solutions (IM) at temperatures down to 100° K, but *not* in rigidly frozen IM solutions at 77° K. In the latter case, the luminescence of the aromatic compounds and their reaction with the solvent to produce substituted hexatrienes[4] are also suppressed. No new u.v. absorption appears on melting the solution, and none that might be attributed to bicyclic intermediates, charge-transfer or radical ions has yet been detected. However, on cooling the IM solutions from 90° to 77° K, the vibrational band system associated with the $A^1B_{2u} \leftarrow X^1A_{1g}$ transition of the benzene rings is progressively replaced by a new system displaced to the blue region by ~140 $cm.^{-1}$. The effect is reversible; it can also be promoted by addition of $CHCl_3$, (but not C_2Cl_4 or CCl_4), and becomes increasingly pronounced with increased methylation of the benzene ring. With hexamethylbenzene and $CHCl_3$, the shift is ~450 $cm.^{-1}$. The narrow temperature range over which the phenomenon occurs suggests a kind of phase change, and it can be attributed to the formation of a regularly oriented aggregate with the nature of a microcrystal. The blue shift is consistent with an effect which has been termed "packing strain", in the oriented solvation shell around the aromatic ring.[5] Its onset heralds the suppression of the production of tetraenes from the chloro-olefins.

TABLE

Wavelengths of principal maxima of adducts formed from benzene

Chloro-olefin		λ_{max} (mμ)		
$C_2H_2Cl_2$	Exptl.	292	306	322
(all 3 isomers)	Calc.	294	306	318
C_2HCl_3	Exptl.	299	313	328
	Calc.	302	314	326
C_2Cl_4	Exptl.	305	320	335
	Calc.	310	322	334

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