Photochemical Transformations of the Benzene Ring

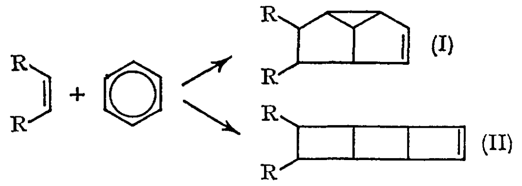
By D. BRYCE-SMITH
(*Chemistry Department, Reading University*)
and H. C. LONGUET-HIGGINS
(*University Chemical Laboratory, Cambridge*)

IN recent years the following photochemical reactions of the benzene ring have been reported.

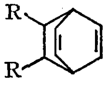
(*a*) Ultraviolet irradiation of liquid benzene gives fulvene but no other benzene isomers;[1]

(*b*) 1,2,4- and 1,3,5-Tri-t-butylbenzene give mixtures of bicyclohexadiene ("Dewar-benzene"), benzvalene, and prismane isomers; intermediates of this type have been reasonably postulated to account for certain positional isomerisations of other alkylbenzenes.[2]

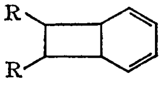
(*c*) Irradiation of a liquid mixture of benzene and a mono-olefin gives two kinds of adduct, (I) and (II)[3]:



Adducts of types (II′) and (II″) do not seem to be formed by olefins.[4] [Intermediates of type (II″) apparently are formed in the addition of some dienophiles, but in such cases direct excitation of the benzene ring is not the primary process.[5]]



(II′)

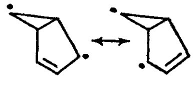


(II″)

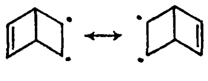
(*d*) With conjugated dienes—1,4-addition appears to occur across the *para*-positions of the ring.[6]

The first step in each of these reactions seems to be the photoexcitation of benzene to its lowest excited singlet state, of species ${}^1B_{2u}$.[7] One would expect the only excited states of appreciable lifetime to be this state and the lowest triplet state, of species ${}^3B_{1u}$.[8] Here we shall attempt to interpret the foregoing observations in terms of these two states alone.

In reaction (*c*) no fulvene is formed.[3b] This strongly suggests that the precursor of (I) is an active species which can either attack the olefin or isomerise, more slowly, to fulvene. The structure of (I) suggests that this is a biradical of structure (III).



(III)



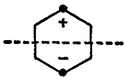
(IV)

This biradical has the interesting property that its lowest electronic configuration is antisymmetrical about its symmetry plane; the ${}^1B_{2u}$ state of benzene is likewise antisymmetric about the plane through any opposite pair of carbon atoms. An orbital correlation diagram[9] shows that the latter state can pass adiabatically into the singlet form of (III), and a rough calculation indicates that the process is slightly exothermic.

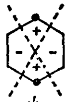
The immediate precursor of (II), on the other hand, would appear to be a biradical of type (IV). The lowest configuration of (IV) would be antisymmetrical about the plane bisecting the terminal bonds; the ${}^3B_{1u}$ state of benzene is likewise antisymmetric about the plane bisecting any opposite pair of C–C bonds. The 1,4-addition (*d*) would, however, suggest another biradical, of type (V), and the lowest triplet state of such a radical would also be antisymmetric about the plane bisecting its double bonds.

(V)

The above canonical structures for (IV) and (V) disguise a close relation of both to the ${}^3B_{1u}$ state of benzene. This state, which may well be formed by intersystem crossing from the initially formed ${}^1B_{2u}$ state,[8c] has two components in its wave function. One of these, corresponding to the excitation of an electron from ψ_3 to ψ_4,



ψ_3

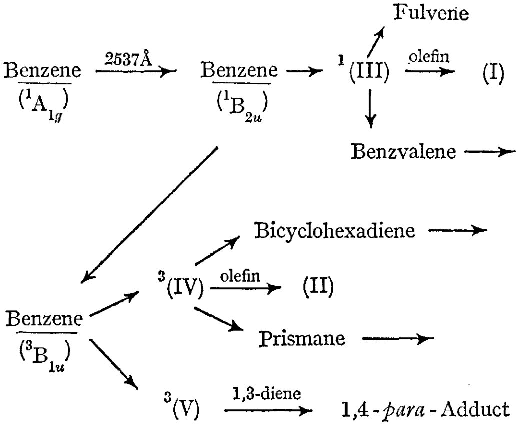


ψ_4

will be stabilised by a distortion which brings the marked carbon atoms nearer together. Electron resonance studies indeed show that the ${}^3B_{1u}$ state distorts spontaneously.[8b] The above component correlates adiabatically with the lowest triplet states of both (IV) and (V), whereas neither of these can be correlated adiabatically with the benzene ${}^3B_{2u}$ state. The triplet forms of (IV) and (V) can thus be regarded as tautomers of ${}^3B_{1u}$ benzene, and the singlet form of (III) as a tautomer of ${}^1B_{2u}$ benzene.

The formation of species of type (III) accounts readily for the formation of benzvalene derivatives in the absence of olefins. (That benzvalene is not formed from benzene itself may be due to its photosensitised decomposition.) Likewise, the formation of prismanes may be attributed to the electrocyclisation of species of type (IV), without invoking the intermediacy of unexcited bicylohexadienes. The 1,4-addition of butadienes to (V), and the failure of mono-olefins to add across its *para*-positions, is in accord with the Woodward–Hoffmann rules for one-step photochemical additions,[10] and suggests that the addition of (IV) or (V) to an unsaturated hydrocarbon is indeed a single-step process.

These proposals are summarised in the following scheme:



Two predictions follow. First, we must presume that in the photolysis of pure benzene at 2537 Å benzvalene, prismane, and bicyclohexadiene are formed but continuously destroyed. The reconversion of benzvalene into benzene could lead to 1,2-shifts, whereas that of prismane could lead to 1,2- and 1,3-shifts; reconversion of bicyclohexadiene would cause no permutation of ring atoms. These shifts could be detected by isotopic labelling (*cf.* refs. 2, 11). Secondly, although the production of fulvenes, benzvalenes, and 1,3-adducts does not require triplet intermediates, triplet species should be involved in the formation of the other products.

(*Received, July* 21*st*, 1966; *Com.* 528.)

---

[1] (a) J. M. Blair and D. Bryce-Smith, *Proc. Chem. Soc.*, 1957, 287; H. J. F. Angus, J. M. Blair, and D. Bryce-Smith, *J. Chem. Soc.*, 1960, 2003; (b) D. Bryce-Smith and J. E. Lodge, unpublished work; I. Haller, *J. Amer. Chem. Soc.*, 1966, **88**, 2070, quoting unpublished work with R. Srinivasan.

[2] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1965, **87**, 4004, and references quoted therein.

[3] (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1966, **88**, 2066; (b) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Comm.*, 1966, 512, and references quoted therein.

[4] A. Gilbert and B. H. Orger, unpublished work.

[5] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 1962, 2675; D. Bryce-Smith and M. A. Hems, *Tetrahedron Letters*, 1966, 1895; G. S. Hammond and W. M. Hardham, *Proc. Chem. Soc.*, 1963, 63.

[6] K. Koltzenburg and K. Kraft, *Tetrahedron Letters*, 1966, 389; and private communication.

[7] A. L. Sklar, *J. Chem. Phys.*, 1937, **5**, 669.

[8] (a) S. Leach and R. Lopez-Delgado, *J. Chim. phys.*, 1964, **61**, 1636; P. G. Russell and A. C. Albrecht, *J. Chem. Phys.*, 1964, **41**, 2536; (b) M. S. De Groot and van der Waals, *Mol. Phys.*, 1963, **6**, 545; (c) H. Ishikawa and W. A. Noyes, *J. Amer. Chem. Soc.*, 1962, **84**, 1502.

[9] H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 1965, **87**, 2045.

[10] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2046.

[11] A. W. Burgstahler and P. L. Chien, *J. Amer. Chem. Soc.*, 1964, **86**, 2940.