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THE ORGANIC PHOTOCHEMISTRY OF BENZENE—I

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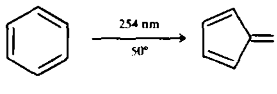
INTRODUCTION

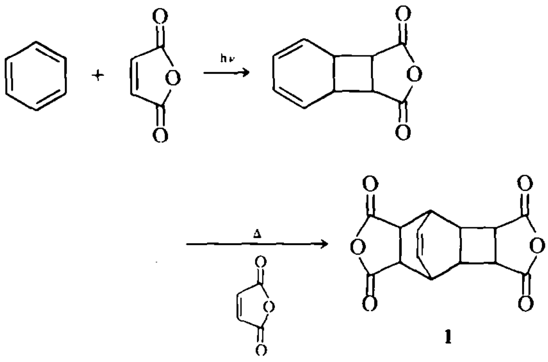
This is Part I of a two-part review of the photochemistry of the benzene ring, and is largely concerned with photoisomerisation reactions, whereas Part II will mainly cover photo-addition and -substitution processes. It has however been found convenient to include the orbital symmetry aspects of photoadditions in this first Part in view of the mechanistic relationships which exist between some photoisomerisation and photoaddition processes, for example those involving the formation of a *meta*-bond.

Our special interest in the photochemistry of benzene arose from a fortuitous observation made some 20 years ago at a time when benzene was widely reported to be stable to UV radiation. Isopropylbenzene was being used as a trap for radicals produced by the reaction $RLi + RHal \rightarrow 2R. + LiHal$ (an unusual homolytic process[1] subsequently rediscovered by the CIDNP technique), and an independent low-temperature source of free alkyl radicals in solution was required for comparison. UV irradiation of RI, R_2Hg, and R_4Pb in isopropylbenzene proved most satisfactory; but a control experiment in which isopropylbenzene was irradiated alone gave traces of a mysterious highly unsaturated yellow product, apparently an isomer of isopropylbenzene since it could not be concentrated by fractional distillation. Then benzene itself was found to photoisomerise to fulvene, and the mystery was solved.[2] The photoprocess was also unusual in being temperature dependent.



This hitherto unsuspected lability of the benzene ring stimulated considerable research interest in the area, and has posed interesting mechanistic and theoretical problems. Many of the subsequent findings have been as surprising as the original formation of fulvene.

For example, early attempts to trap the rather unstable fulvene as a Diels–Alder adduct by irradiating benzene in the presence of maleic anhydride led with great serendipity not to the expected adduct, but to an entirely novel and surprisingly stable 2:1 photoadduct of maleic anhydride and benzene (1) which was suggested to arise by sequential photochemical and thermal addition steps as follows.[3]



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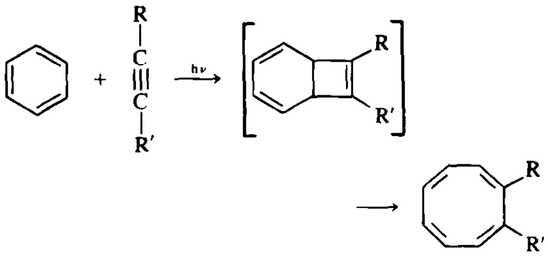
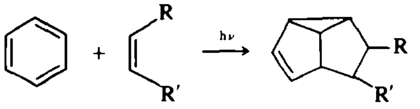
The reaction can be photosensitised by benzophenone.[4]

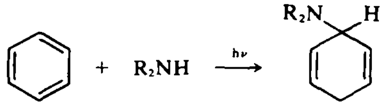
The proposed initial 1,2-cycloaddition of maleic anhydride suggested that the use of an acetylenic dienophile should give a cyclo-octatetraene; and so it transpired.[5,6]



Since then, numerous other photoadditions to benzene have been reported, notably the surprisingly efficient 1,3-cycloadditions of simple alkenes discovered independently by two groups,[7,8]



and the synthetically useful photoadditions of primary, secondary, and tertiary amines,[9] for example



The list of photoaddends to benzene now includes alkenes, alkynes, dienes, water, alcohols, diethyl ether, ketones, carboxylic acids, amines, pyrroles and furan: photo-oxidation and -reduction have also been observed.

Other milestones were provided by American workers who showed that benzene photoisomers other than fulvene could be produced by direct irradiation, notably benzvalene (2)[10] and, from t-butyl-substituted benzenes, Dewar benzenes[11] and prismanes.[12]

Thus the photochemistry of benzene has proved to be much more varied than the thermal chemistry. In general, whereas most of the thermal (electronic ground state) reactions produce *aromatic* products by substitution processes, the photoreactions generally give *non-aromatic* products by either isomerisation or photoaddition. Of course, there are exceptions to this generalisation, such as thermal catalytic hydrogenation and photoelectrophilic substitution, but these are less common. The ready formation of non-aromatic photoproducts doubtless arises in part from the great excess of the quantal energy for the $S_0 \rightarrow S_1$ transition (*ca.* 460 kJ mole^{-1}) over the classical resonance energy for benzene (*ca.* 150 kJ mole^{-1}). Likewise, the energy available from the quantum permits *meta*-bonding leading to the formation of unstable and highly strained systems such as benzvalene which would normally be difficult or impossible of direct access from benzene by thermal routes.

The various photoprocesses are now discussed in more detail. Emphasis is placed on the organic photochemistry of benzene itself, and of substituted benzenes in which the aromatic ring itself undergoes transformation. Heterocyclic aromatic systems are not covered, except where their behaviour is closely relevant to that of benzenes. Extensive references to the more physical aspects of benzene photochemistry will be found in the annual volumes of Ref. 13, but the electronic symmetry properties of the ground and excited states of benzene will now be discussed as they are of direct mechanistic relevance to the reactions under consideration.

Symmetry aspects

The UV absorption spectrum of benzene (Fig. 1) shows considerable vibrational fine-structure which is more detailed and well-defined for the vapour than for the liquid, and tends to be less marked in substituted derivatives than in the parent hydrocarbon, especially if the substituent bears p or π orbitals which overlap with π orbitals of the ring. The three bands shown correspond to electronic excitation from the ground state S_0 to the first three excited states S_1, S_2 and S_3. The $S_0 \rightarrow S_1$ transition (λ_{max} 254 nm; ϵ 204 l mole^{-1} cm^{-1}) is from the totally symmetric ground state ($^1A_{1g}$) to the S_1 state ($^1B_{2u}$) which is antisymmetric with respect to a plane perpendicular to the molecular plane and passing through an opposite pair of carbon atoms, as for the transition densities depicted in Fig. 2. Although it is formally "forbidden" and therefore of low intensity, this is in fact the transition most commonly involved in the photoreactions of benzene. It occurs as a result of breaking of the "forbiddenness" through molecular deformations of the ring which change the symmetry. Intersystem crossing from the S_1 state to the T_1 state can occur, but although it has the high triplet energy of 355.64 kJ mole^{-1} (*ca.* 85 kcal mole^{-1}) T_1 benzene seems to be involved in comparatively few photoreactions other than as a sensitiser, e.g. for the *cis-trans* isomerisation of alkenes. This process applied to but-2-ene forms the basis of Cundall's method for estimating the quantum yields of formation of T_1 benzene,[14] and has even (using xylene rather than benzene) been applied to the direct preparation of *trans*-cyclo-octene, from the readily available *cis*-isomer.[15] It is noteworthy that T_1 benzene ($^3B_{1u}$) has electronic symmetry properties similar to those of S_2 benzene ($^1B_{1u}$).

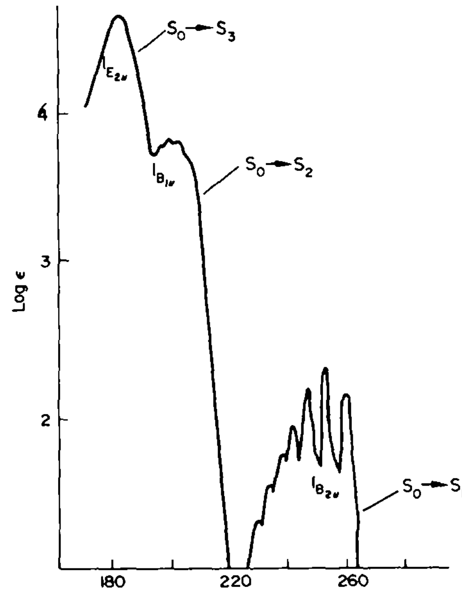


Fig. 1. Ultraviolet spectrum of benzene.

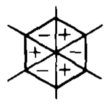


Fig. 2. S_1 benzene ($^1B_{2u}$).

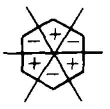


Fig. 3. S_2 benzene ($^1B_{1u}$).

The S_2 state of benzene is formed from the ground state by the second optical transition shown in Fig. 1 (λ_{max} 203.5 nm; ϵ 7400 l mole^{-1} cm^{-1}). This transition, like the $S_0 \rightarrow S_1$ transition, is also formally 'forbidden'. From an electronic viewpoint, S_2 benzene is antisymmetric about a plane perpendicular to the molecular plane which bisects an opposite pair of bonds as shown in Fig. 3. It is known that S_1 benzene is a planar regular hexagon,[16] but S_2 and T_1 benzene may be distorted.[17-19]

The third transition, $S_0 - S_3$ ($A_{1g} \rightarrow E_{1u}$), is formally allowed and the absorption is therefore very intense (λ_{max} 180 nm; ϵ 60,000 l mole^{-1} cm^{-1}). Being on or near the transmission limit of fused quartz, it has not so far proved to play much part in benzene photochemistry. An excellent and more detailed discussion of the symmetry properties of excited states of benzene has been given by Salem.[19]

The state symmetries shown in Figs. 2 and 3 were first used by Bryce-Smith and Longuet-Higgins[20] to provide theoretical analyses of photoreactions of benzene, and subsequently by Hoffmann and Woodward[21] and Haller.[22] For example, the non-planar diradical (3)† termed "prefulvene",[20] which would be formed by *meta* bonding in benzene, has in its ground state an electronic configuration which is antisymmetrical about its molecular symmetry plane in the manner of S_1 benzene (Fig. 2).

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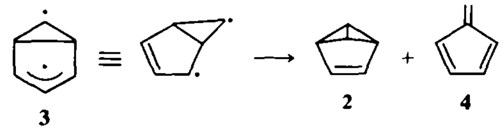
†Diradical 3 has also been discussed by I. Jano and Y. Mori, *Chem. Phys. Letters* **2**, 185 (1968), but their suggestion that singlet and triplet forms of it are in equilibrium appears to have no justification.



Following the correlation principle first enunciated by Longuet-Higgins and Abrahamson,[23] it is to be expected that S_1 benzene should be potentially *meta*-bonding and capable in principle of undergoing an adiabatic transformation into the ground state of the prefulvene diradical (**3**): this diradical in turn is readily conceived as a precursor of both fulvene (**4**) and benzvalene (**2**). By such reasoning, one is led to conclude that if fulvene and benzvalene arise by processes which initially involve the formation of a *meta* bond in benzene, these isomers may be derived from S_1 benzene, as is indeed found experimentally.[24] We shall later see that benzvalene can also be formed from S_2 benzene by a fully concerted process not involving prefulvene as an intermediate.

It is instructive and helpful also to consider orbital rather than state symmetries.

The orbital symmetries of benzene are depicted in Fig. 4.

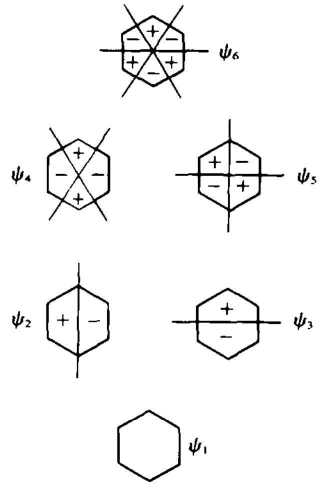


Fig. 4. Orbital symmetries of benzene.

Let us first consider S_1 benzene. This state, of symmetry $^1B_{2u}$, has two components in its wave-function, one corresponding to the excitation of an electron from ψ_3 to ψ_5, and the other to excitation from ψ_2 to ψ_4. [It will be noted that combination of the *orbital* symmetries of ψ_3 and ψ_5, and ψ_2 and ψ_4, gives the S_1 *state* symmetry (Fig. 2)]. The S_1 (B_{2u}) state is represented as $\psi_3\psi_5 - \psi_2\psi_4$. Likewise, the S_2 or T_1 states of symmetry B_{1u} are represented as $\psi_3\psi_4 + \psi_2\psi_5$. Although the S_1 and S_2 states each involve partial occupancy of the degenerate orbital pairs ψ_2, ψ_3 and ψ_4, ψ_5, the energy of the S_2 state lies well above that of the S_1 state (Fig. 1).

We may now construct an orbital correlation diagram for *meta*-bonding in benzene: this is shown in Fig. 5.

The correlation diagram is constructed in the normal manner, expressing the orbitals as symmetrical (S) or antisymmetrical (A) with respect to the molecular symmetry plane, and avoiding forbidden crossings of correlations between orbitals of like symmetry. It is readily seen that the ground state of the prefulvene diradical (π_2 and p each singly occupied) correlates uniquely with the S_1 state of benzene through the $\psi_2\psi_4$ component of the latter. Since $\psi_2\psi_4$ and $\psi_3\psi_5$ are equally part of the wave function of S_1 benzene, either can serve to establish a valid correlation with orbitals in the non-aromatic product. Thus we have reached the same conclusion as that reached previously by consideration of state symmetries, namely that *meta*-bonding in benzene is a property associated with the S_1 state, of symmetry $^1B_{2u}$. However, it is a property of S_1 benzene that carbon atoms C_1 and C_3 are non-bonding in the equilibrium molecular conformation[25] a planar regular hexagon, of side slightly larger than S_0 benzene),[16] but tend to become bonding when brought closer together by an appropriate disrotatory distortion of the ring structure.[24] Thus both electronic and vibrational factors must be involved in *meta*-bonding.

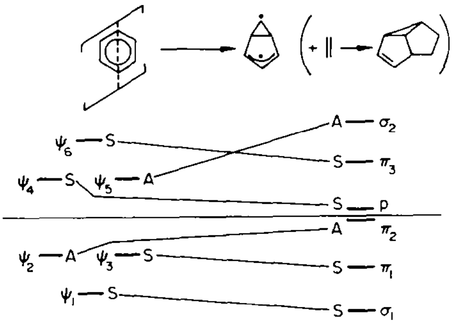


Fig. 5. *meta*-Bonding in benzene.

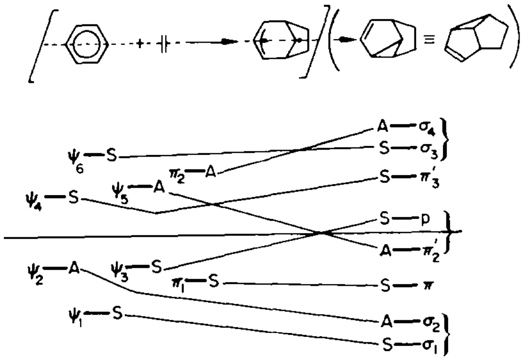


Fig. 5*a*. 1,3-Addition of ethylene to benzene.

It may be seen from a comparison of Figs. 5 and 5a that the formation of 1,3-adducts with alkenes can proceed from S_1 benzene + S_0 alkene either *via* prefulvene or as a concerted direct *meta*-addition of the alkene. This point will be further discussed in Part II.

para-Bonding can be considered in a similar manner, and shown to be a characteristic of the S_2 rather than the S_1 state. The orbital symmetry diagram is shown in Fig. 6.

It may be seen that correlation with a low excited state of Dewar-benxene (bicyclo[2,2,0]hexa-2,5-diene), or the ground state of the corresponding *para*-diradical uniquely involves the $\psi_3\psi_4$ component of S_2 benzene. The further point may be made that although the potential *para*-bonding in $S_2(^1B_{1u})$ and $T_1(^3B_{1u})$ benzene may cause these molecules to distort spontaneously,[20] the potential *meta*-bonding in S_1 $(^1B_{2u})$ benzene does not apparently do so to a measurable degree,[16] and for the reason indicated above should require a thermal activation step (or formation at a high vibrational level) to produce significant deformations which have the effect of bringing *meta* positions closer together. We shall see later that there is experimental evidence for such thermal or vibrational activation in *meta*-bonding.

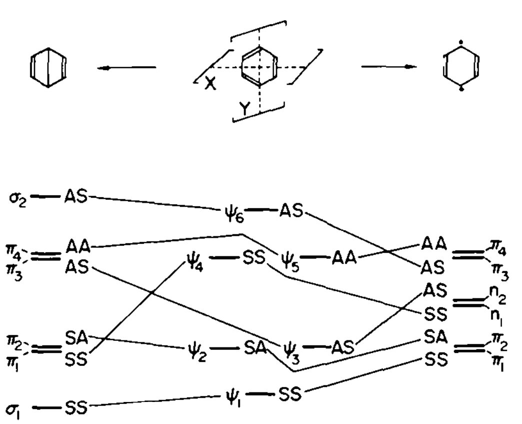


Fig. 6. *para*-Bonding in benzene.

Although we have already considered the formation of benzvalene (**2**) in a two-stage process from S_1 benzene via intramolecular cyclisation of prefulvene (**3**), there is also reason to believe that benzvalene can arise by an alternative route from S_2 benzene via a species formally resembling *cis, cis, trans*-cyclohexatriene, the so-called "Möbius-benzene".[26] The corresponding correlation diagram shown in Fig. 7 indicates the possibility of an adiabatic transformation of S_2 benzene ($\psi_2\psi_5$ component) into S_1 benzvalene by this route. It is therefore very satisfactory that benzvalene has indeed been found to be produced from S_2 benzene; the process differs from that which proceeds from S_1 benzene in that there is no evidence for a thermal (vibrational) activation stage.[27] Note that disregarding the electronic symmetry properties of the intermediate would have produced the misleading conclusion that the thermal rearomatisation of benzvalene is a symmetry-allowed process.

An orbital symmetry approach similar to that used above for photoisomerisations has also been applied to the problem of concerted cycloadditions to the benzene ring.[28] This has led to the interesting conclusion that the Woodward–Hoffmann Rules are not generally applicable to photoadditions to the benzene ring. Professor Hoffmann has indeed kindly informed one of us (D.B.-S.) that he has reached a similar conclusion in several cases from a rather different analysis; and it should be borne in mind that the classic monograph on the conservation of orbital symmetry[29] is concerned almost wholly with transformations of non-aromatic systems. Of course, the principle of conservation of orbital symmetry applies as strongly to photoreactions of benzene as to those of non-aromatic molecules, but the degeneracy of ψ_2 and ψ_3, and ψ_4 and ψ_5 in benzene coupled with the fact that all four of these orbitals are partially occupied in the S_1, S_2 and S_3 states of benzene produces a situation without parallel in non-aromatic systems, and one in which the simple Rules derived for such systems may fail to apply. Figures 8 and 9 exemplify this statement for the cases of *ss* and *sa* 1,2-photoadditions of ethylene to benzene.[30] Note that non-Hückel levels are used for ethylene, e.g. π_2 ethylene is placed at higher energy than ψ_4 and ψ_5 benzene, in acknowledgement of the experimental fact that the energy of S_1 ethylene is higher than that of S_1 benzene. With substituted benzenes and/or ethylenes, the effect of the substituent may be to bring π_2 ethylene below ψ_4 and ψ_5 benzene. Thus if the spacing of energy levels is such that the lowest energy excitation is $\pi_1 \rightarrow \pi_2$, the correlation diagram must be correspondingly altered so as to apply to the addition of S_1 ethylene to S_0 benzene. In Fig. 8 for example, π_2 could now correlate with π_2', and ψ_5 with π_4', and the addition becomes allowed as a concerted process (see Table 1, cases 1 and 2). Likewise, if the relative energy levels are such that the lowest energy transition is $\pi_1 \rightarrow \psi_4, \psi_5$ (i.e. donor ethylene) or $\psi_3, \psi_4 \rightarrow \pi_2$ (donor benzene), the system will be one where photoexcitation can in principle proceed by charge-transfer. For charge-transfer absorption to occur to a significant extent in practice, it is probably necessary for the benzene and the ethylene to form a suitably oriented "dark" molecular complex in solution so that some degree of interpenetration of orbitals on the donor and acceptor molecules is provided prior to photoexcitation. Where this prior complexing condition is not adequately met, there remains the possibility of "contact" charge transfer. But

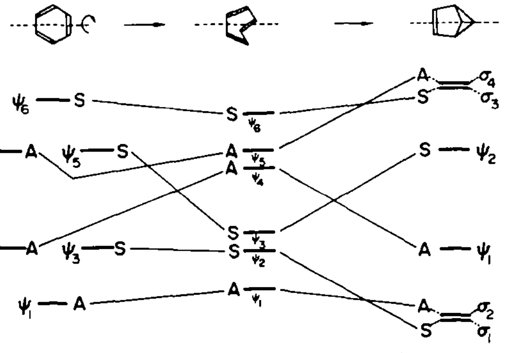


Fig. 7. Concerted formation of benzvalene from benzene.

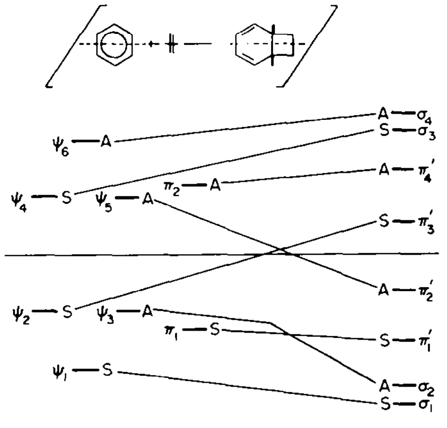


Fig. 8. *ss* 1,2-Photoaddition of ethylene to benzene.

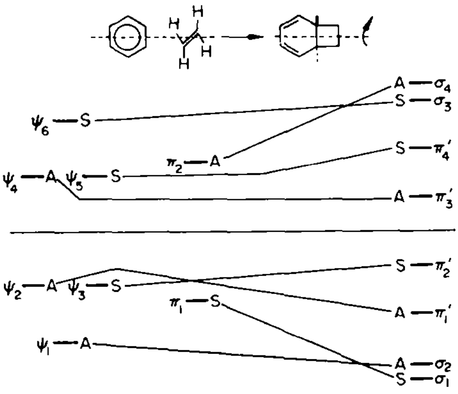


Fig. 9. *sa* 1,2-Photoaddition of ethylene to benzene.

Table 1. Orbital symmetry relationships for concerted cycloadditions to the benzene ring[28]

	Addend	Addition mode	Product	Excited species			Charge-transfer excitation		Thermal Reaction
				Addend (S_1, T_1)*	Benzene		Donor Addend	Donor Benzene	
					B_{2u} (S_1)	B_{1u} (S_2, T_1)			
1	Ethylene	cis-ortho/cis-1, 2-	(5)	A	F	A[a]	A	A	F
2	Ethylene	trans-ortho/cis-1, 2-	(6)	A	F	A	A	A	A
3	Ethylene	meta/cis-1, 2-	(7) [→(7a)]	A	A	F[b]	A	A	F[c]
4	Ethylene	para/cis-1, 2-	(9)	A	F	A[d]	A	A	A
5	Ethylene	para/trans-1, 2-	(9)	A	A	A	A	A	F
6	cis-Butadiene	cis-ortho/cis-1, 4-	(10)	A	F[e]	A	A	A	A
7	cis-Butadiene	meta/cis-1, 4-	(11) [→(11a)	A	A	F[b]	A	A	F[f]
8	cis-Butadiene	para/cis-1, 4-	(13)	A	F	A[a]	A	A	F
9	cis-Butadiene	para/trans-1, 4-	(13)[g]	A	A	A	A	A	A
10	trans-Butadiene	para/cis-1, 4-	(14)	A	A	A	A	A	F
11	Benzene	exo-cis-1, 2-cis-1', 2'-	(15)	-	F	A	A		F
12	Benzene	endo-cis-1, 2-cis-1', 2'-	(16)	-	F	A	A		F
13	Benzene	cis-1, 2-1', 4'-	(17)	-	F[e]	A	A		A
14	Benzene	cis-1, 4-1', 4'-	(18)	-	F	A	A		F

* Strictly, the relations apply to a T_1 addend only when this is reacting in an effectively planar conformation. T_2 Benzene may be of state $^3E_{1u}$ (S. D. Colson and E. R. Bernstein, J. Chem. Phys., 1965, 43, 2661). Mixing will occur between states similar in symmetry (e.g. S_1 ethylene and S_2 benzene) if the energies are close.

a Correlation noted also by Hoffmann and Woodward (ref. 21). Professor Hoffmann (personal communication) has reached similar conclusions about the relationships in case 1 from a somewhat different type of analysis,

b Correlation with first excited state of diradical product ;

c Correlation with zwitterion (8);

d The B_{1u} component which apparently permits concernted para—additions of ethylene corresponds to a transition between orbitals ψ_2, ψ_5 which each have zero amplitude at the reaction centres. Nevertheless, the addition should still be possible in principle because the ψ_3 ψ_4 and ψ_2 ψ_5 components are equally part of the B_{1u} state ,

e Allowed correlation with S_2 adduct, which might be accessible in practice ,

f Correlation with zwitterion (12).

g It is possible to envisage the production of adduct (14) by this mode of addition , but Professor R. Hoffmann (Personal communication) has suggested convincingly that adduct (13) should be a preferred product.

charge transfer can occur after photoexcitation, and either to or from the photoexcited molecule: this produces an exciplex intermediate.

We return now to the specific cases represented by Figs 8 and 9.

According to the Woodward–Hoffmann Rules, *ss* and *sa* stereochemical variants of a thermal or photo-reaction cannot both be equally allowed as concerted processes. The fact that these reactions of S_1 benzene with S_0 ethylene are both forbidden as concerted processes, and the reactions of S_2 benzene with S_0 ethylene both allowed, results not from any breakdown in the principle of conservation of orbital symmetry, but rather from the circumstance that S_1 and S_2 benzene each have two pairs of orbital components both of which are equally part of the electronic state involved, and either of which can serve to provide a valid correlation with the appropriate orbitals in the non-aromatic product. Note however that the analysis of the *thermal* reactions gives conclusions in accord with the Woodward–Hoffmann Rules.

Other examples of this orbital symmetry treatment will be found in Part II. The conclusions from analyses of fourteen photoadditions to benzene are summarised in Table 1.[28] It will be seen later in Part II of this Review that some of these conclusions have proved to be of predictive value.

In concluding this discussion of symmetry factors, we draw attention to Haller's analysis of state symmetry relationships in the photoisomerisation of benzene,[22] and to Dougherty's interesting perturbation MO treatment of 1,3-cycloaddition of alkenes to benzene.[31] The latter procedure treats the process as of a "G-type" whereby reaction starts on an excited potential energy surface and proceeds directly to a bonding ground-state configuration by a Born–Oppenheimer violation. The perturbation MO analysis in general is really an extension of the Dewar–Evans rule that thermal and photochemical pericyclic processes proceed via aromatic and antiaromatic transition states respectively. Dougherty suggests that 1,3-adducts (**7a**) tend to be formed because the analogous π-electron system (**19**) is more PMO antiaromatic than the systems (**20** and **21**) used as analogues for 1,2- and 1,4-cycloadditions to benzene respectively. The PMO analysis may well appear at first sight more realistic than the orbital symmetry treatment, for although some adiabatic photoprocesses are known (X-type reactions in Dougherty's classification[31]), most photoreactions are considered to be diabatic, i.e. they give products in ground rather than excited states. But for most photoreactions, including photoadditions to benzene, it is still largely unknown at what point along the reaction co-ordinate the products of diabatic processes relax to the electronic ground state. If this point is subsequent to the transition state, as one feels should normally be the case, an orbital symmetry analysis may lead to perfectly valid conclusions.† And as can be seen from Table 1 (cases 1, 3 and 4), essentially the same conclusions are reached from orbital symmetry analysis as from the perturbation MO treatment. We shall discuss in Part II the evidence that polar factors, as yet unconsidered in the PMO treatment, can be of great importance in 1,2-(but not the 1,3-) additions to benzene. Meanwhile, we do not feel able to agree in general with any suggestion that electronic state or orbital symmetries may be unimportant in determining the preferred product-forming processes. It is salutary to reflect how often in chemistry a valid conclusion has been reached by apparently differing routes.

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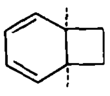
†Thus the transformation of S_1 benzene to S_1 benzvalene, or of S_2 benzene to S_1 Dewar-benzene, would be endothermic, as pointed out by D. W. T. Griffith, J. E. Kent and M. F. O'Dwyer, *J. Mol. Spectrosc.* **58**, 436 (1975). A similar and equally superable difficulty arises in the classic case of photodimerisation of ethylene to cyclobutane, where S_1 cyclobutane is energetically inaccessible.



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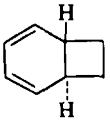

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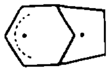

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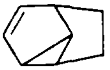

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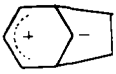

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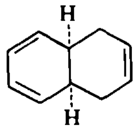

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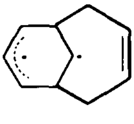

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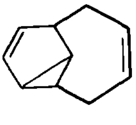

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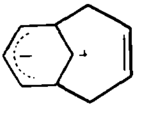

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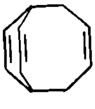

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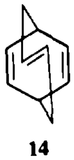

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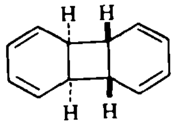

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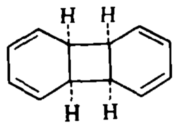

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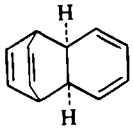

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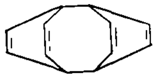

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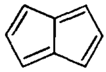

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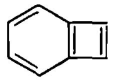

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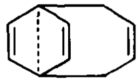

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PHOTOISOMERISATION OF THE BENZENE RING

(a) *Unsubstituted benzene*. Irradiation of liquid benzene at 254 nm populates the S_1 state (Fig. 1), and gives a mixture of fulvene (4)[1,32] and benzvalene (tricyclo$[3.1.0.0^{2,6}]$hex-3-ene) (2),[33-35] but no trace of Dewar-benzene. The quantum yields are *ca.* 0.01–0.03. The formation of both fulvene and benzvalene from neat benzene is promoted by increase of temperature, and at 50–60°, limiting concentrations of *ca.* 300–500 mg l^{-1} of each isomer are obtainable from neat benzene. The chemical yields of both isomers tend to increase with increased dilution of the benzene with an alkane such as hexadecane,[33] although the limiting concentration of fulvene is approached the more slowly–observations which suggest that some or even all of the fulvene may arise from isomerisation of benzvalene, e.g. through catalysis by quartz.[34] The concentrations of both isomers may also be increased by fractional freezing.[2,33] Lutz and Stein have reported a quantum yield of 0.18 for the formation of benzvalene from benzene in O_2-free dilute solution in hexane; they found this to be independent of temperature over the range 9–50°, unlike the situation with undiluted benzene.[36] The reported absence of a temperature effect is rather surprising, and some confirmation of this work might be desirable.†

Fulvene is fairly stable in dilute solution, but it has such a strong tendency to polymerise in more concentrated solutions that it is doubtful whether it has ever been isolated in the pure state.[37] However, it has a characteristic UV absorption spectrum (λ_{max} 365, 242 nm: the tailing of the former peak into the visible is responsible for the marked yellow colour) and was identified by comparison with the spectrum of authentic material prepared from cyclopentadiene and formaldehyde, and by its crystalline thermal adduct with maleic anhydride.[37]

Benzvalene is more acid-sensitive, but less base-sensitive, than fulvene. Its reversion to benzene is strongly sensitised by triplet benzene,[34] and it slowly rearomatises thermally at room temperature with a half-life of about 10 days. Identification was based on its NMR spectrum‡ and upon the thermal reaction with methanolic hydrogen chloride to give methoxy-[3.1.0]bicyclohexenes, mainly (**22a**) plus (as was later shown)[35] minor amounts of (**22b**). Adducts of this type are also formed by direct irradiation of benzene in CF_3CH_2OH or methanolic HCl[33,38] in a process which in a formal sense amounts to 1,3-photoaddition of the alcohol to benzene; but it should be noted that the acid-catalysed addition of methanol to benzvalene is actually a thermal process, and that the methanol merely serves as a trap for photochemically formed benzvalene. Thus the quantum yield for the 1,3-photoaddition of methanol to benzene is within experimental error equal to that calculated for the formation of benzvalene.[39] Acetic acid and even water (as aqueous phosphoric acid) likewise give 1,3-photoadducts,[40] and benzvalene is also a precursor of these (see also Ref. 41).

It is interesting in this connection that a simple *thermal* synthesis of benzvalene from cyclopentadiene has since been described by Katz *et al.*[42] The compound is explosive in the pure state, but safe in solution. Its ready

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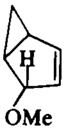
†Dr. K. E. Wilzbach informs us that he is unable to endorse the report in Ref. 36 that the formation of benzvalene is independent of temperature over the range 9–50°. In cyclohexane, he has measured quantum yields at 9°, 25° and 50° of 0.035, 0.05 and 0.08 respectively; but the values in water were 0.06, 0.07 and 0.07 respectively.

‡The UV spectrum of benzvalene is unusual, and shows a characteristic series of bands at 2172, 2182, 2212, 2222, 2256 and 2266 Å.[34]



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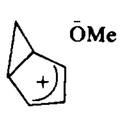
22b



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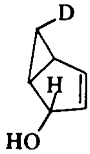

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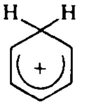

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availability by a thermal route has led to intensified investigation of its chemistry, and in particular has provided confirmation of its intermediacy in the photohydration of benzene: the use of D_2O gave **23**, thereby confirming Berson and Hasty's suggestion[41] that benzvalene rather than the benzenonium ion (**24**)[43] is the key intermediate in the acid-catalysed 1,3-photohydration of benzene. The bicyclo[3.1.0]hex-3-en-2yl cation (**25**) was proposed as an intermediate in the photoadditions of methanol and other hydroxylic compounds to benzene,[43] and its formation via protonation of photochemically generated benzvalene under strongly acidic conditions has since been demonstrated.[35] Under less strongly acidic conditions, increasing proportions of the *endo* adducts, e.g. (**22b**), are formed, probably via a non-dissociating ion-pair, e.g. (**22c**). Other isomeric products are formed by benzene-sensitised vinylcyclopropane rearrangement of the primary adducts (**22a** and **b**).[35]

As we have seen, only fulvene and benzvalene appear to be formed on irradiation of liquid benzene at 254 nm, and there is still some uncertainty whether some of the fulvene arises from S_1 benzene by a route independent of benzvalene or whether it all results from isomerisation of benzvalene. The absence of Dewar-benzene following excitation in the $S_0 \rightarrow S_1$ band contrasts with its formation in significant amounts when liquid benzene is irradiated at shorter wavelengths.

Thus irradiation of liquid benzene using an oxygen lamp emitting in bands over the 165–200 nm range gave the isomers Dewar-benzene, fulvene, and benzvalene, in the ratio 1:2:5, plus a small amount of biphenyl.[44] Irradiation of benzene vapour under similar conditions gives no benzvalene (contrary to two erroneous reports[45]), or Dewar-benzene, but mainly fulvene and the open-chain isomer *cis*-(and thence by photoisomerisation *trans*-)-hexa-1,3-dien-5-yne:[46] higher pressures favoured the formation of fulvene whereas lower pressures favoured the hexadienynes.[46] Although the authors of Refs. 46*c*, *d* suggested that the liquid-phase process involved vibrationally excited upper electronic excited states of benzene, and the gas-phase process vibrationally excited ground states, the effect of phase on the production of Dewar-benzene and benzvalene is perhaps more economically explained in terms of the relatively low thermal stability (→benzene) of these isomers. One might suppose that they are formed in both the liquid- and vapour-phase processes, and in upper vibrational states. In the liquid phase the excess of vibrational energy would be rapidly lost by collision so that these thermally unstable molecules would soon attain thermal equilibrium and thereby have some chance of survival. In the vapour-phase, and especially at low pressures, vibrationally "hot" Dewar-benzene and benzvalene would have a far lower frequency of collision with other molecules and therefore a greater tendency for thermal rearomatisation. The survival of fulvene in the vapour-phase process is likewise explicable, for it is not a particularly thermally unstable molecule *per se*, unlike Dewar-benzene and benzvalene, but rather tends to be lost by polymerisation; which process is not expected to be very efficient in the vapour phase. The genesis of the hexadienynes is not fully understood, but the pressure dependence mentioned above coupled with studies of the direct irradiation of fulvene vapour[46b] suggest that they arise at least partly from vibrationally and/or electronically excited fulvene. It is interesting that fulvene photoisomerises to benzene at 254 nm in the vapour phase[46b] but not in the liquid phase.[32]

The formation of Dewar-benzene on irradiation at 165–200 nm leaves open some interesting questions of mechanism, for both S_2 ($^1B_{1u}$) and S_3 ($^1E_{1u}$) states of benzene would be populated under these conditions, and thence quite possibly the T_1 ($^3B_{1u}$) state and other triplet species. It has in fact been shown by selective irradiation into the $S_0 \rightarrow S_2$ band of benzene, and the use of a triplet trap, that S_2 benzene is the precursor of Dewar-benzene.[47] The reaction is strongly promoted by dilution with cyclo-octane or cyclo-octene. This reaction provided the first known example of a non-dissociative chemical transformation from an upper singlet state. The result, though unusual, is nicely in harmony with the orbital symmetry analysis in Fig. 6, and provides gratifying confirmation of earlier predictions.[20,48]

It is interesting in this connection that Braun *et al.*[49] had found some years earlier that the efficiency of internal conversion from upper electronic states to the S_1 state (which is normally unity for most organic molecules that have been studied in dilute solution) is significantly less than unity in the case of benzene and some methylbenzenes. We may now reasonably attribute at least part of the discrepancy to a tendency for 1,4-bonding in the S_2 state of benzene, just as 1,3-bonding (Fig. 5) provides a corresponding mechanism for energy loss in S_1 benzene.†

It now remains to consider the mechanism by which benzvalene is formed following $S_0 \rightarrow S_1$ excitation of benzene. We may with some confidence exclude T_1 benzene formed from the S_1 state by intersystem crossing, for benzvalene is readily formed on irradiation of benzene vapour at 237 nm (at which wavelength benzene triplets appear to be virtually absent) and its formation is *promoted* by *cis*-but-2-ene, a strong quencher of triplet benzene:[14] the promoting effect seems likely to result from competition by the quencher with the very efficient triplet benzene sensitised decomposition of benzvalene.[34]

We may also exclude benzene excimers as necessary precursors of benzvalene since the formation of this isomer from benzene is promoted by dilution with an alkane. This exclusion leaves us to consider S_1 benzene at various vibrational levels. While it is in fact clear from the accumulated evidence that benzvalene is derived from S_1

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†We suggest that the long-mysterious "Channel 3" often postulated to account for the quite efficient radiationless disappearance of vibrationally excited S_1 benzene, and currently attributed to $S_1 \rightarrow S_0$ internal conversion, may well involve *meta*-bonding followed by rearomatisation of the prefulvene diradical directly and/or via benzvalene. It is odd that the ability of S_1 benzene to undergo *meta*-bonding has been almost wholly overlooked in the extensive discussions in the photophysical literature relating to this subject (see also the results in Table 2).

benzene, much evidence also points to the need for vibrational excitation of this state.

Thus the temperature dependence of the formation of both benzvalene and fulvene in the liquid phase suggests the need for thermal activation. This idea of vibrationally excited S_1 benzene is supported by Kaplan and Wilzbach's observation that the quantum yield of benzvalene from benzene vapour increases with decreasing wavelength of irradiation within the $S_0 \rightarrow S_1$ band (Table 2); but it is a little unexpected that the yield in solution was essentially independent of wavelength between 238 and 254 nm:[34] (*cf.* Ref. 36). This latter result appears to suggest that the formation of benzvalene from S_1 benzene in the liquid phase requires at most only a modest degree of thermal activation. A similar wavelength effect has been reported for the photoisomerisation of benzene-1,3,5-d_3 to the 1,2,4-isomer via an assumed benzvalene intermediate, and it was concluded that at least three-quarters of the isomerisation at 248 nm arose from vibrationally excited S_1 benzene.[39]

Table 2. Quantum yields of photoprocesses in benzene vapour[34]

	253 nm	245 nm	242 nm	237 nm
Benzvalene $^{\underline{a}}$	0.016	0.022	0.024	0.037
Benzene butene photo-adduct $^{\underline{a}}$	0.01	0.005	0.006	0.003
Fluorescence $^{\underline{b}}$	0.18	0.10	0	0
Triplets $^{\underline{b}}$	0.6	0.6	small	

$^{\underline{a}}$ 1 atm. of cis-but-2-ene, 25 torr of benzene.

$^{\underline{b}}$. From data in ref. 14b. Alkenes cause little or no quenching of benzene fluorescence unless they bear substituents which confer marked donor or acceptor character relative to benzene.

Thus the vapour phase results as a whole suggest that formation of benzvalene occurs most readily at high vibrational levels of S_1 benzene, and the decrease of fluorescence quantum yield with decreasing excitation wavelength[14b] would be consistent with the idea that formation of prefulvene, benzvalene, and fulvene completes increasingly with fluorescence deactivation of S_1 benzene at the higher vibrational levels. The formation of benzvalene would also seem to become more competitive with the cycloaddition to butene as the vibrational level of S_1 benzene is raised: this observation is consistent with the proposal[8] that both benzvalene and the 1,3-cycloadducts with alkenes can arise from prefulvene as a common precursor. To summarise, it is evident that benzvalene and fulvene derive from S_1 benzene by processes which appear to proceed most efficiently from vibrationally excited levels, especially in the gas phase.

We refer now to the remarkable thermal stability of both benzvalene and Dewar-benzene. Dewar and Kirschner give $\Delta H = -85$ kcal mole^{-1} for rearomatisation of benzvalene,[50] (a figure which may be a little on the high side) and rearomatisation of Dewar-benzene is only slightly less exothermic. Although both isomers tend to detonate in the pure liquid state, the fact that they can be isolated at all at ambient temperatures indicates that their thermal reversions to benzene can only occur by highly activated routes, and further suggests, but does not prove, that the reactions are "forbidden" as concerted processes on orbital symmetry grounds. Dewar and Kirschner have indeed calculated an activation energy of 21.5 kcal mole^{-1} for the rearomatisation of benzvalene, and have rather surprisingly described the process as "allowed" while asserting that the molecules do not possess enough symmetry for orbital correlations to be applied.[50] These workers do not consider either aromatisation via the prefulvene diradical (**3**) or the alternative intermediate formation of *cis, cis, trans*-cyclohexatriene (**26**; "Möbius-benzene": see Figs. 7 and 10). This latter high-energy species would also be the product of ring-opening of Dewar-benzene by a conrotatory twist.

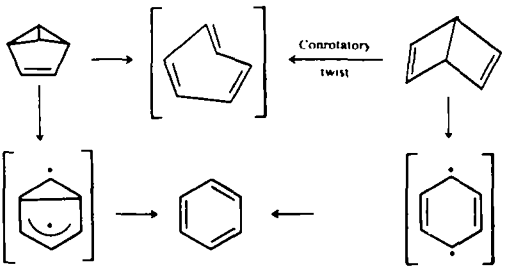

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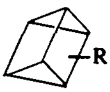
Fig. 10. Aromatisation of benzvalene and Dewar-benzene.

Such considerations (*pace* Dewar and Kirschner) appear to provide a qualitatively satisfactory explanation for the degrees of thermal stability shown by these isomers.

The main features of the pattern of benzene photoisomerisation reactions are summarised in Fig. 11.

PHOTOISOMERISATION OF SUBSTITUTED BENZENES

The general harmony between theory and experiment which prevails in the case of unsubstituted benzene is not always so immediately apparent when we come to consider the behaviour of substituted benzenes; yet even with these, and allowing for certain gaps in our knowledge, close examination reveals little discordance. The isomerisation reactions observed fall into two main categories, (i) formation of fulvenes, benzvalenes, Dewar-benzenes, and prismanes (**27**), and (ii), formation of positional isomers involving *apparent* migration of a substituent, e.g. *o*-xylene→*m*-xylene. In fact, there is evidence that benzvalenes, etc. are involved as intermediates in processes of type (ii). We shall return later to this point, but at this stage we shall concentrate on isomerisation processes of type (i).



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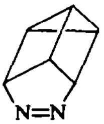

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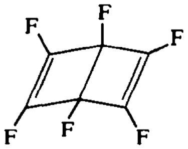

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Hexafluorobenzene. In marked contrast with benzene, hexafluoro-Dewar-benzene (hexafluorobicyclo[2.2.0]-hexa-2,5-diene) (**29**) is the only isomer formed on irradiation of hexafluorobenzene in the liquid or vapour phase at wavelengths over the range 212–265 nm.[22,52-54] Irradiation of solutions of hexafluorobenzene in cyclohexane and cyclo-octane gives hydrogen fluoride and a complex mixture containing cyclohexylpentafluorobenzene and other radical coupling products, but no photoisomers are obtained.[55]

Hexafluoro-Dewar-benzene (**29**), m.p. 6°, b.p. 52°, is highly explosive in the pure liquid state (as is benzvalene)

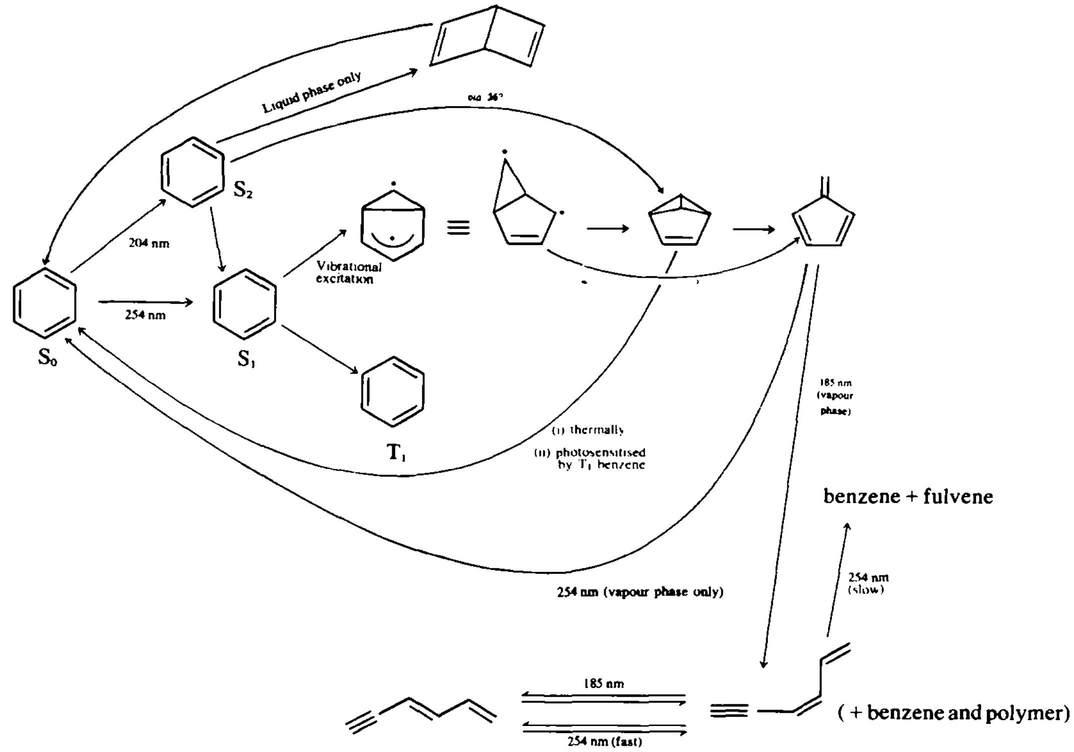


Fig. 11. Photoisomerisation reactions of benzene. *Note.* The formation of unsubstituted prismane (27: R = H) by photoisomerisation of benzene has not yet been observed, but substituted prismanes are formed from some benzene derivatives (see next section). Katz and Acton have synthesised prismane in low yield by photoelimination of nitrogen from the azo-compound (**28**). It is a thermally stable liquid at room temperature, but isomerises to benzene at 90° ($t_{1/2}$ = 11 h.)[51]

but can be handled safely in solution. It rearomatises smoothly to hexafluorobenzene in the vapour phase at 80°.

The photochemical formation of the Dewar isomer at 248 nm is apparently a singlet process (Hg and Ph_2CO do not photosensitise, O_2 and *cis*-but-2-ene do not inhibit) and is promoted by the presence of inert gases such as nitrogen. This latter effect has been ascribed to collisional deactivation of the initially formed and vibrationally "hot" Dewar isomer.[22] But if rearomatisation of the vibrationally excited Dewar isomer were the only factor which restricts the apparent (i.e. measured) quantum yields for its formation, one might expect these quantum yields to fall with decreasing wavelength of the exciting radiation. The effect observed is shown in Table 3, which is based on data given in Ref. 22.

Inspection of the trends shown in Table 3 suggests that the measured quantum yields are determined by at least two factors. Thus the intrinsic quantum yield clearly increases with decreasing wavelength over the range 265–230 nm, whereas the measured quantum yield is highest at 248 nm and tends to fall off markedly at both longer and shorter wavelengths. One might conclude from these results that the measured quantum yields are a resultant of two opposing tendencies, one an increase in the efficiency of formation of the Dewar isomer with increasing quantal energy over the indicated wavelength range, and the other an increase in the rate of rearomatisation of this photoproduct with increase in its initial vibrational level. If this picture is correct, the peak in measured quantum yield at or around 248 nm arises from optimisation of the result of these opposing tendencies.

But in view of the behaviour of benzene itself (Fig. 6), we must also consider whether transformation to the Dewar isomer takes place not from the S_1 state, but from a higher singlet state. Comparison of the absorption

Table 3. Effect of wavelength on the quantum yield for formation of hexafluoro-Dewar-benzene

	265 nm	248 nm	229 nm	212 nm
Measured quantum yield (mean)[*]	0.019	0.036	0.019	0.006[≠]
Intrinsic quantum yield[**]	0.0207 ± 0.0013	0.0463 ± 0.0031	0.081 ± 0.014	

[*] The mean values given here are calculated from results obtained with N_2 as diluent at pressures of 834 - 843 mm, and are similar to the means of all corresponding values measured over a much wider pressure range.

[**] This is defined as the quantum yield which would be observed if all the vibrationally 'hot' molecules escaped decomposition.

[≠] One measurement.

spectrum of hexafluorobenzene (Fig. 12) with that of benzene (Fig. 1) shows that the S_1 and S_2 states are much closer in energy in the case of the fluoro-compound, and the corresponding absorption envelopes overlap to a much greater extent. The data in Table 3 would be qualitatively in agreement with the idea that Dewar-benzene results from excitation within the $S_0 \rightarrow S_2$ band (κ_{max} 231 nm) rather than $S_0 \rightarrow S_1$ (λ_{max} 254 nm).

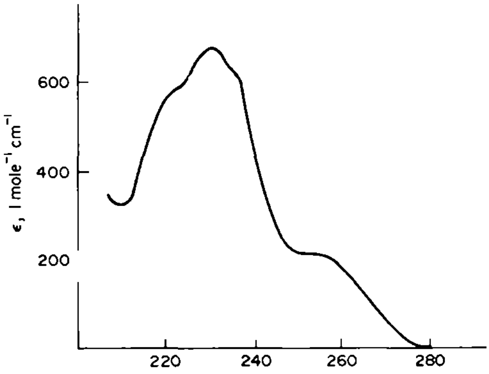


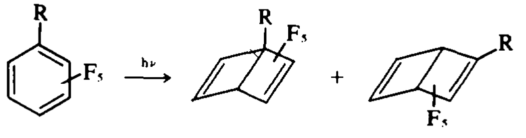
Fig. 12. Ultraviolet absorption spectrum of hexafluorobenzene.

If the ordering of states is the same in hexafluorobenzene as in benzene (and this remains to be proved: but see Phillips[56]), transformation to the Dewar-isomer could be occurring from the S_2 ($^1B_{1u}$) or S_3 ($^1E_{1u}$) states. Both processes are symmetry-allowed.[20,21,48] The idea that an upper excited singlet state is involved in the formation of hexafluoro Dewar-benzene is supported by the results of a study by Phillips of the photophysical properties of hexafluorobenzene.[56] He concluded that excitation at wavelengths shorter than 280 nm gives rise to two excited singlet states. One of these rapidly decays to the fluorescent state (the lowest vibrational level of the S_1 state), whereas the other (an upper vibrational level of the S_2 state?) appears to undergo an efficient isomerisation process, presumably 1,4-bonding. The fluorescence spectrum of hexafluorobenzene does not vary with the wavelength of the exciting radiation, but the fluorescence quantum yields do so vary, although they are very low ($\Phi_f \leq 0.02$).[22]

Thus there are strong indications that the seemingly anomalous formation of hexafluoro Dewar-benzene (**29**) results from 1,4-bonding in the S_2 state—a symmetry-allowed concerted process if this state is of $^1B_{1u}$ symmetry, as with benzene (Fig. 6). It remains to be explained why hexafluorobenzvalene and hexafluorofulvene are not also obtained via the S_1 state. Formation of the fulvene would involve a 1,2 fluorine-shift, and such processes are much less common than those involving hydrogen. Possibly the as yet unknown hexafluorobenzvalene is formed but is too thermally or photochemically unstable to survive the experimental conditions so far employed. If this is the explanation, it might possibly prove to be detectable following irradiation through the $S_0 \rightarrow S_2$ band of hexafluorobenzene in glasses at very low temperatures, or in the gas-phase at 1 atm. with an excess of N_2 or CO_2 as vibrational quenchers.†

Other fluorobenzenes. The tendency for *para*- rather than *meta*-bonding which is apparent in hexafluorobenzene is also observed in a number of the lower fluoro-derivatives.

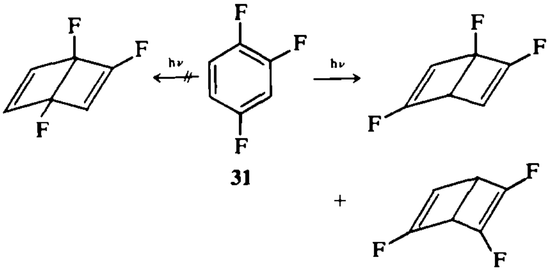
Thus Ratajczak found that some, but not all, substituted pentafluorobenzenes reacted as follows:



30: R = H, CH_3, OCH_3, CF_3

In contrast, the corresponding compounds (**30**) in which R=Cl or $-CH=CH_2$ gave no photoisomers.[58]

In another study, 1,2,4-trifluorobenzene (**31**) gave two of the three possible Dewar isomers, but no fulvenes, benzvalenes, or hexadienynes were found.[59]



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Quantum yields were in the range 2×10^{-4}–1×10^{-3}, depending on the conditions.

Although there is no specific evidence to implicate the triplet state of 1,2,4-trifluorobenzene in the photoisomerisation, other workers[60] have reported that the energy of the T_1 state lies below that of *cis*-but-2-ene: the triplet yield was 0.4. The triplet yield of monofluorobenzene (measured by sensitised emission from biacetyl) is even higher at 0.67–0.93, depending on the wavelength of the exciting radiation,[61] but it is rather surprising that no photoisomers have yet been detected following irradiation of this compound.

Haszeldine *et al.* have reported some most interesting studies on the isomerisation of perfluoroalkylbenzenes, notably **32** and **33**. Their most remarkable observation is undoubtedly the *thermal* isomerisation of (32) to the Dewar-isomer (**34**) at 400° with a contact time of 1 s.[62] The isomer (**34**) undergoes rearomatisation when heated for 6 hr at 140°. Its formation at the higher temperature is clearly determined by kinetic rather than thermodynamic control and might well involve the transient formation of a non-planar *para*-diradical (**35**) with concomitant relief of strain due to overcrowding: the conditions of rapid quenching employed would presumably permit intramolecular cyclisation to the Dewar-isomer (**34**), a compound more thermally stable than most other Dewar-benzenes which have so far been prepared. An alternative concerted thermal isomerisation would require conrotatory twist at C_1 and C_4 with the formation of a *cis*,

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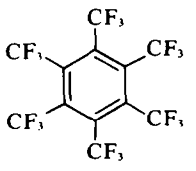
†A Ph.D. Thesis by Y.-C. Wang, University of New Brunswick, 1969 [*Diss. Abs. Int.*, (B) **31**, 1219 (1970)] reports the formation of hexafluoroprismane and hexafluorobenzvalene together with the Dewar isomer on irradiation of hexafluorobenzene at 254 nm. An intermediate having a "two-hour mean life-time" was very speculatively identified as Möbius-hexafluorobenzene. However, the UV spectra attributed by Wang to hexafluoroprismane (λ_{max} 246, 286 nm) and hexafluorobenzvalene [λ_{max} *ca* 220, 230, 252 nm (shoulder)] are so different from those of prismane[51] and hexamethylprismane[57] (extended end-absorption only), and benzvalene[34] (λ_{max} 217, 218, 221, 222, 226 and 227 nm), that they raise serious doubts concerning the identities of the products obtained. This report should perhaps be viewed with some reserve pending the publication of a more convincing account in a scientific journal.



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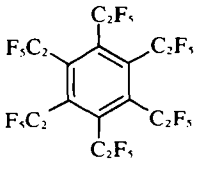

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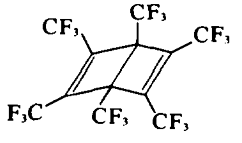

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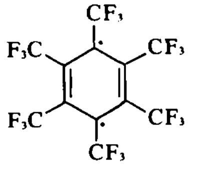

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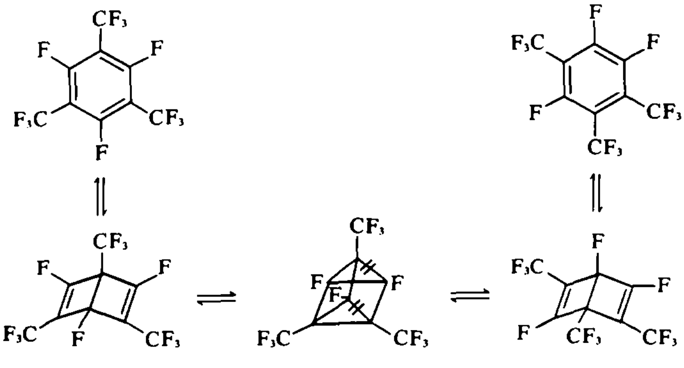
cis, trans-cyclohexatriene system, and can therefore be ruled out with some confidence.

In comparison, the photoisomerisation of 32 leads to formation of the corresponding benzvalene, Dewar-benzene, and prismane derivatives.[63] The ratios of these are time-dependent, owing to interconversions between the isomers. Thus the Dewar-isomer (34) forms the prismane directly, whereas the benzvalene appears to give this indirectly via rearomatisation and further photolysis. However, Lemal *et al.*[64] report that the Dewar-isomer (34) is produced on pyrolysis of the corresponding prismane.

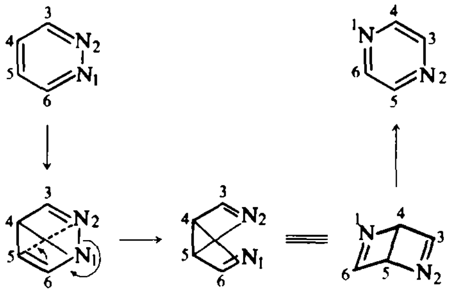
Irradiation of the corresponding pentafluoroethyl compound (33) has been reported to give mainly the prismane, with traces of the Dewar-isomer (presumably a precursor of the prismane): the benzvalene isomer was not detected.[63]

Haszeldine *et al.* have extended the above thermal and photochemical isomerisation studies to the related molecules perfluoropentaethylmethylbenzene and perfluoro-1,2,3,5-tetraethyl-4,6-dimethylbenzene, with broadly similar results.[65] It is abundantly clear that the introduction of perfluoroalkyl substituents greatly increases the ease of formation and thermal stability of Dewar- and prismane-isomers of aromatic rings.

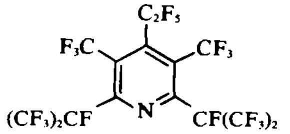
It is particularly interesting that perfluoro-1,3,5- and -1,2,4-trimethylbenzenes have been found by Haszeldine *et al.* to undergo clean vapour phase photochemical (but not thermal) interconversion via intermediate moderately stable Dewar- and prismane-isomers, as shown below.[66] The net effect corresponds to apparent 1,2-shifts of F and CF_3, although it will be seen that the isomerisation involves the transposition of ring atoms rather than the migration of substituents.



The interconversion between the Dewar-isomers via the prismane is relevant to the mechanistic problem of photochemical 1,2-shifts of alkyl groups in alkylbenzenes which is discussed more fully in the next section dealing with these compounds. It is reminiscent of (but distinct from) the observations by Chambers *et al.*[67] that perfluoroalkyl-pyridazines undergo photoisomerisation to the corresponding pyrazines through intermediate *para*-bonded Dewar-type species via the following route corresponding to a formal 1,3-shift of a nitrogen atom.

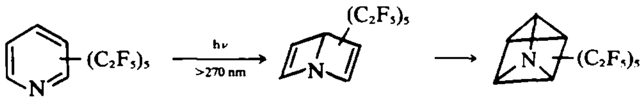


Prior to this work, it had been believed that 1,3-transpositions in aromatic rings involve either prismane-type intermediates or successive 1,2-transpositions. An example of a rearrangement of similar type between two Dewar isomers has also been demonstrated for the pyridine derivative (36),[67] but no homocyclic cases have yet been recognised.

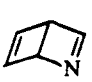


One may also note in passing that the related pyridine derivative (37) gives the corresponding azaprismane (38: $t_{1/2}^{170^\circ} = 1.1$ hr) on irradiation at wavelengths >200 nm, although the remarkably stable Dewar isomer (39: $t_{1/2}^{170^\circ} = 104$ hr) is the major product at wavelengths >270 nm.[68] In contrast, parent pyridine gives the much less stable azomethine Dewar-isomer (40: $t_{1/2}^{25^\circ} = 2$ min) on irradiation at 254 nm in the liquid phase,[69] and at the time of writing (Jan. 1976) neither the isomer (41) nor the parent azaprismane (42) has yet been obtained. More detailed descriptions of the photoisomerisation of pyridines, pyrazines and other aza-aromatic systems will be found in the annual Volumes of Ref. 70, especially Part III, Chap. 4 of Vols. 2, 3, 5 and 6, and in Refs 71 and 72.

Photoisomerisation reactions of alkylbenzenes. Although toluene and other alkylbenzenes having at least



37 **39** **38**



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one α-H atom can undergo C-H homolysis on irradiation in glasses or the solid state at very low temperatures, or on flash photolysis in the gas-phase, to give the corresponding benzyl-type radicals,[73] this process (which may involve absorption of two photons) does not readily occur in the liquid-phase at near-ambient temperatures under normal experimental conditions. One or both of the following reactions can occur on irradiation at 254 nm in the gas or liquid phase:

(i) ring isomerisation to fulvenes, benzvalenes, Dewar-benzenes, prismanes, and the ring-opened dienynes (these are not all necessarily formed in a particular case); cf. Fig. 11;

(ii) positional isomerisation of the alkyl substituents, e.g. $o \rightarrow m$-xylene.

There is a fairly broad measure of agreement that positional isomerisations of type (ii) occur via the intermediate formation and re-aromatisation of valence-bond ring isomers by processes of type (i). But in many cases such intermediates have not yet been detected. Their involvement has been inferred from isotopic labelling studies on mesitylene-1,3,5-$^{14}C_3$ which prove that the 1,2,4-isomer arises exclusively by ring-transposition, and not by methyl group migration.[74] Barltrop and Day (whose proposals are further considered later in this section) have suggested that analysis of type (ii) processes in terms of twelve possible ring-permutation patterns provides an alternative mechanistic approach. However, it will be convenient to consider processes of types (i) and (ii) together at this stage.

The ring transpositions which give rise to apparent 1,2-shifts of alkyl substituents can in principle involve either benzvalene or prismane substituents, whereas those which cause apparent 1,3-shifts involve either prismanes, an isomerisation between Dewar-forms of the type previously discussed for the pyridazine→pyrazine transformation,[67] (and not yet known for benzene derivatives), or photoisomerisation between benzvalenes. The processes are summarised in Fig. 13.

Pathway *a* normally gives rise only to 1,2-transpositions, and thence only to apparent 1,2-shifts of substituents; but photoisomerisation of the initial benzvalene (as is discussed later in connection with tri-t-butylbenzenes) could in principle provide an apparent 1,3-shift *via* pathway *d*(ii). Pathway *b* involves two 1,2-transpositions [C_1C_2 and C_3C_4 in *b*(i)] and thereby can give rise to apparent 1,2- and/or 1,3-shifts depending on the modes of bond-cleavage in the prismane in relation to ring substituents or isotopic labels. Pathway *c* can give rise to 1,3-transpositions only, and therefore only apparent 1,3-shifts of substituents could result.

In addition to the foregoing transformations, at least one example is reported of non-reversible isomerisation of a benzvalene to the Dewar-isomer, viz the hexamethyl derivatives (unpublished results by Ertl and Lokensgard mentioned in Ref. 75).† If this is confirmed to occur, the

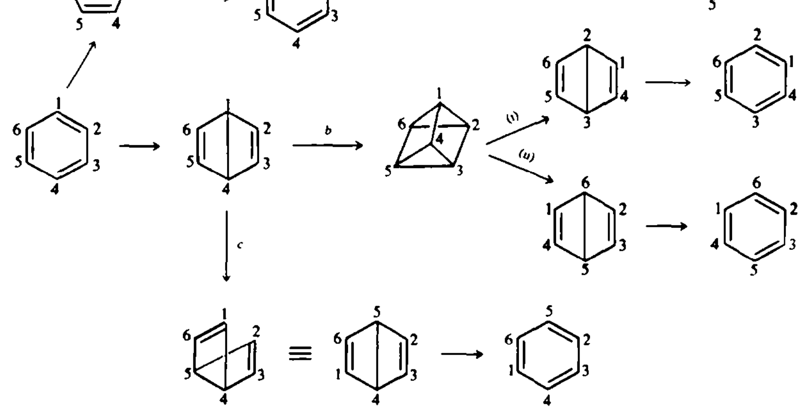

Fig. 13. Pathways for transpositions in the benzene ring.

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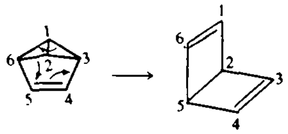
†It is of passing interest that the 1,4-bond in hexamethyl Dewar-benzene is the longest (1.63 Å) known C–C bond [M. J. Cardillo and S. H. Bauer, *J. Amer. Chem. Soc.* **92**, 2399 (1970)].

process will have to be considered as a possibility in other cases, although one may note that benzvalene itself can be produced from benzene without the appearance of any detectable trace of the Dewar-isomer, and Dewar-benzene is not known to isomerise to benzvalene. A process of the following type could be involved.



There is thermochemical evidence that the benzvalene→Dewar-benzene isomerisation would be only slightly exothermic, at least for the hexakis-trifluoromethyl derivatives. For thermal transformations between valence-isomers of benzene derivatives, the absolute energies of the various structures are strongly dependent on the substituents (e.g. through dipole–dipole repulsions), but the relative energy levels are largely independent of the substituents.[75]

As previously noted, the interconversions of perfluoro-1,3,5- and 1,2,4-trimethylbenzenes appear to provide examples of the 1,2-mode of pathway *b* in Fig. 13. The 1,3-mode may not have been observed because it would have produced either no apparent change or the somewhat more overcrowded 1,2,3-isomer. Likewise, although pathway *c* is at present only known to be followed in the cases of certain pyridines and pyridazines,[67] there seems no reason in principle why it should not be available for benzene derivatives: it would for example provide a considerable relief of strain in cases where C_1 and C_2 bore bulky substituent groups such as t-butyl. However, there is certainly evidence that pathway *a* is preferred in the photoisomerisation of 1,3,5- to 1,2,4-tri-t-butylbenzene, as further noted below, and it has quite often been invoked for other systems even in the absence of specific evidence.

Dialkylbenzenes. Wilzbach and Kaplan were the first workers to describe the photochemical interconversion of the isomeric xylenes,[76] and Burgstahler and Chien almost simultaneously reported the photoisomerisation of di-t-butylbenzenes.[77] van Tamelen *et al.* subsequently published similar findings with di-t-butylbenzenes which they had obtained at about the same time.[78] The xylenes underwent isomerisation in the gas-phase, or in the case of *m*-xylene rather less efficiently in "isohexane" solution or as the pure liquid. It was demonstrated that the primary methyl shifts are exclusively 1,2 in character: the traces of *p*-xylene formed on prolonged irradiation of the *o*-isomer evidently arose by re-isomerisation of the first-formed *m*-isomer. The quantum yield for conversion of *o*- to *m*-xylene in the gas phase was 0.012. Although radicals are known to be formed by photolysis of xylenes,[79] it was demonstrated that the photoisomerisation did not involve radical dissociation followed by recombination, and only minute traces of toluene were formed. On the other hand, irradiation of ethereal *o*-di-t-butylbenzene gave a 1:4 photostationary equilibrium mixture of the *m*- and *p*-isomers respectively, with total disappearance of the strained *o*-isomer, and the same photostationary proportion also resulted when either of the *m*- or *p*-isomers was used as starting material.[77] Despite the apparently major 1,3-shift in the *o*-isomer, it is apparent that most if not all of the *p*-isomer arose by a double 1,2-shift; so the situation does not appear to differ fundamentally from that with *o*-xylene.

The mechanism of 1,2-methyl shifts in xylenes has received considerable attention, and differing proposals have been advanced. Thus Ward compared the vapour-phase photolysis of *o*-xylene at 254 nm with that in the vacuum ultraviolet region at 160–210 nm, and reported that toluene, *m*-xylene, *p*-xylene and *o*-ethyltoluene were formed in each case, but that the products of vacuum-UV photolysis also included a little benzocyclobutene.[80] He concluded from this result and from fluorescence measurements that highly vibrationally excited electronic ground states of the xylene are most likely to be involved as common intermediates, and rejected both the S_1 or higher singlet states, and the T_1 state, as alternative candidates. However, it became apparent from work of Ward and Barta[81] on the behaviour of deuterium-labelled xylenes and the effects of gaseous D_2 that the experimental conditions employed were conducive to the dissociation of benzylic C–H bonds and that "hot" hydrogen atoms so formed added to xylene molecules with expulsion of methyl radicals which in turn gave rise to various other products. It is very difficult to distinguish the products which might have arisen by such free radical processes from those which might have arisen through non-dissociative ring transpositions. Nevertheless, the major individual product was *m*-xylene both in this study and in the earlier work of Wilzbach and Kaplan.[76] The idea that some limited isomerisation of xylenes can occur via "hot" ground state molecules is lent support by the report of Crow and Wentrup[82] that 1,2-shifts occur to a very small extent on pyrolysis of xylenes; but Ward[80] found no *m*- or *p*-xylene among the products of flow pyrolysis of *o*-xylene at 580°, so the position concerning the involvement of "hot" electronic ground state molecules in the vapour-phase photoisomerisations remains a little obscure.

On the other hand, Cundall *et al.* have reported evidence which appears strongly to implicate an upper vibrational level of the S_1 state in the photoisomerisation of *o*- to *m*-xylene in isopentane solution at 254 nm.[83] They observed (*a*), that *trans*-but-2-ene in amounts sufficient to quench all the aromatic T_1 species had little effect on the formation of *m*-xylene or on fluorescence from the S_1 state, and (*b*), that xenon (which quenches the S_1 state by promoting intersystem crossing through a heavy-atom effect†) suppressed both the fluorescence and the formation of the *m*-isomer: both these latter quenchings had the same Stern–Volmer constants. The observed effect of dilution also ruled out any route involving the formation of an excimer.

It is interesting that Anderson found the quantum yields for isomerisation of *m*-xylene to the *o*- and *p*-isomers in hexane, perfluorohexane, or EPA to increase with temperature over the range −10 to 80°C. Both processes had an activation energy of 4.7 kcal $mole^{-1}$ (a value close to the 7 kcal $mole^{-1}$ found for isomerisation of S_1 benzene to benzvalene[27]), and the *ortho*:*para* ratio was independent of the reaction parameters.[84] Although the quantum yields at 248 and 275 nm were the same in this solution study, Noyes and Harter reported that the quantum yields for photoisomerisation of the three xylene isomers in the gas-phase increase with decreasing wavelength down to ca. 240 nm.[85] This difference presumably results from the

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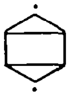
†It has also been shown that the quantum yield for formation of triplet benzene increases from *ca* 0.5 to unity in the presence of xenon [R. B. Cundall and W. Tippett, *Trans. Faraday Soc.* **66**, 350 (1970)].

more effective collisional deactivation of vibrationally excited S_1 states in solution, and in conjunction with the observed effect of temperature,[84] again points to the need for thermal (vibrational) excitation before an S_1 aromatic can undergo intramolecular *meta*-bonding,[48] an important point we have already discussed in connection with the isomerisation of S_1 benzene to the prefulvene diradical, benzvalene, and fulvene.

The foregoing evidence accords with the postulate that the 1,2-shifts observed in the xylenes are mostly a result of ring transpositions rather than the migration of methyl groups, and that these transpositions largely and perhaps exclusively involve rearomatisation of dimethylbenzvalenes according to pathway *a* in Fig. 13.

A slight mechanistic uncertainty does however remain over the origins of the traces of *p*-xylene liable to be formed from *o*-xylene. Wilzbach and Kaplan[76] reported that the *para* isomer was not formed at low conversions in the gas-phase, and one is bound to infer that the small amounts produced at higher conversions arose by secondary isomerisation of *m*-xylene, although in this case a 1,3-shift would not of course lead to isomerisation. The position may be slightly different in solution in that traces of the *para* isomer ($m/p \sim 13$) appear to be formed even at low conversion (footnote 12 in Ref. 74). Cundall, Robinson and Voss[83] suggested that *p*-xylene might arise from *o*-xylene via an intermediate diradical of type (**43**). This seems rather improbable as an intermediate since orbital symmetry analysis indicates that its formation from the S_1 aromatic would be highly forbidden as a concerted process. The comparative rarity of direct 1,3-transposition processes in benzene and its derivatives may in general be deemed to result from the absence of a direct symmetry-allowed one-quantum route via the S_1 state (compare Figs. 5, 6, 11 and 13).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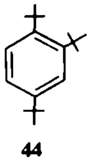
It may be noted in passing that "*para*"-bonding and 1,3-shifts are relatively common among aromatic nitrogen heterocycles where excited states may have $n\pi^*$ character, but such compounds are beyond the scope of this Report. Numerous examples are however described in the annual Volumes of Ref. 13.

Photoisomerisation of tri-t-butylbenzenes. In a striking example of creative reasoning, van Tamelen and Pappas argued that the presence of two bulky *ortho*-substituents in an aromatic ring might favour the formation of the non-planar Dewar-isomer by twisting of the bond between the substituents. They accordingly irradiated 1,2,4-tri-t-butylbenzene (**44**) and were able to identify the less overcrowded Dewar-isomer (**45**) among the products.[86]

A more extensive study of the tri-t-butylbenzenes was subsequently reported by Wilzbach and Kaplan from which it transpired that the benzvalene and prismane isomers are also formed.[87] These had not been obtained in the earlier study,[86] possibly owing to an unfortunate choice of work-up procedures.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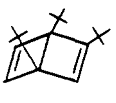
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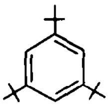
The behaviour of 1,3,5- and 1,2,4-tri-t-butylbenzenes shows some interesting differences. Thus irradiation of the 1,3,5-isomer (**46**) in "isohexane" at 254 nm gives 1,2,4-tri-t-butylbenzvalene (**47**) as the only initial product, with a quantum yield of 0.12. Continued irradiation led to aromatisation of the benzvalene (**47** to **44** and **46**), and the fulvene (**48**), Dewar-benzene (**45**), the isomeric benzvalene (**49**), and the prismane (**50**). In sufficiently dilute solutions, a photostationary state was reached in which the prismane (**50**) was the major component, partly no doubt because it was the least strongly absorbing species.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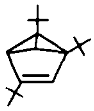
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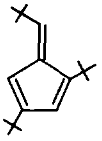
On the other hand, the 1,2,4-isomer (**44**) gave the Dewar-isomer (**45**), as previously reported,[86] together with 1,3,6-tri-t-butylbenzvalene (**49**), both possibly as primary products.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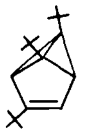
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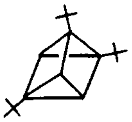
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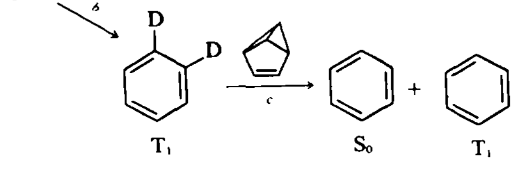
The mechanism of the photochemical interconversion of the isomeric benzvalenes (**47** and **49**) is as yet unknown, but the transformation appears to proceed directly rather than via an intermediate aromatisation stage and may involve a vinylcyclopropane valence-bond isomerisation of the type envisaged by Viehe when he originally named this class of compounds.[88] A similar interconversion of benzvalenes was subsequently shown to occur with benzvalene-d_2 as follows:[88a]



Pathway *a* is followed on direct irradiation, the use of pyrene as a singlet sensitiser, or the use of a triplet sensitiser having $E_T < 65$ kcal mole^{-1}: pathway *b* is favoured by the use of triplet sensitisers of energy higher than this. The triplet sensitised processes *a* and *b* may involve T_1 and T_2 benzvalene respectively. It is interesting that the quantum yields for pathway *b* are higher than unity, in accordance with the chain process *c*.

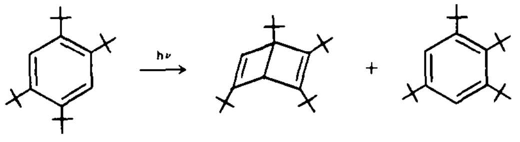
Whereas the unstrained 1,3,5-tri-t-butylbenzene (**46**) appears to form only a benzvalene as the primary product, as with benzene itself, and in accord with the 1,3-bonding mechanism already discussed, the overcrowded 1,2,4-tri-t-butylbenzene (**44**) also forms a significant amount of a Dewar-isomer (**45**). If this latter is indeed a primary photochemical product, its formation from the S_1 state of **44** would be expected to be forbidden as a concerted process on orbital symmetry grounds if one assumes that the analysis for benzene itself can be extended to this overcrowded derivative. So one may conclude either that it arises from the S_2 state of the aromatic, as with benzene and hexafluorobenzene, or that it is formed from the S_1 state in a non-concerted process, possibly via the T_1 state. It is apparent from comparison of the UV absorption spectra that irradiation at 254 nm would populate only the S_1 state of **46**, but both the S_1 and S_2 states of (**44**):[89] the UV spectrum of *o*-di-t-butylbenzene is very similar to that of **44**.[90] However, the formation of **45** at *ca.* 280 nm[87] could not involve the S_2 state to any significant extent.

Although the work on tri-t-butylbenzenes by van Tamelen on the one hand,[78,86] and Wilzbach and Kaplan on the other[87] is of great importance, close study of the reports reveals several areas of uncertainty and statements for which no experimental evidence has yet been published, so we deem it prudent to restrict any mechanistic discussion to the foregoing limited remarks. In particular, it might be unwise to draw too close comparisons between the photochemical behaviour of the tri-t-butylbenzenes under conditions favourable to direct rather than photosensitised excitation of the benzvalene, etc. photoproducts, with the behaviour of benzene itself under conditions in which triplet benzene-sensitised decomposition (largely aromatisation) of the parent benzvalene is a more important process.

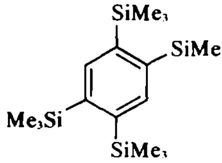
The above work may be compared with Arnett and Bollinger's report that 1,2,4,5-tetra-t-butylbenzene (**51**) gives the 1,2,3,5-isomer (**52**) and the corresponding Dewar form **53**.[91] Again it appears that overcrowding of t-butyl substituents tends to favour the production of Dewar isomers rather than benzvalenes.

Irradiation of the corresponding trimethylsilyl compound (**54**) in ether or 2-methylbutane has been shown by West *et al.* to produce the 1,2,3,5-isomer (**55**), the benzvalenes (**56** and **57**), and two fulvenes [one of structure **58**].[92] This behaviour resembles that of **51** in the formation of **55**, and differs from it in the formation of benzvalenes (**56** and **57**) and the apparent failure to produce Dewar isomers. The absence of these latter isomers might well result from a lower degree of ring distortion in **54** than in **51** (the Si–C bond being much longer than C–C), in accord with the previous comments concerning the behaviour of tri-t-butylbenzenes.

1,2-*Photochemical shifts of substituents in other systems.* The general, if not exclusive, tendency for 1,2-shifts noted in the foregoing sections has also been observed in 2-, 3- and 4-tritylanisoles,[93] bitolyls,[94] monomethylbiphenyls,[95] 2-, 3- and 4-fluorobenzotrifluorides[96] and 2,6-di-t-butyphenols.[97] In most of these cases, benzvalenes have been postulated though not isolated as intermediates. Zimmerman and Crumrine have obtained evidence that photoracemisation of the optically active biphenyl (**59**) occurs by two mechanisms, only one of which appears to involve benzvalene intermediates.[98] Exceptionally, Matsuura *et al.*[97] have shown that photoisomerisation of the di-t-butylphenol (**60** to **61** and **62**) occurs by a triplet mechanism involving intermediate keto-tautomers of the phenol rather than benzvalenes. The use of ArOD gave a mixture of *o*- and *p*-deuteriated products, in accordance with this mechanism. A "*para*" keto-tautomer (**63**) was actually isolated following irradiation of the phenol (**64**). Irradiation of anisole gives *m*-cresol, possibly via a bicyclohexenone formed from a keto-tautomer of *p*-cresol.[99]



51 **53** **52**



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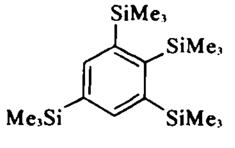

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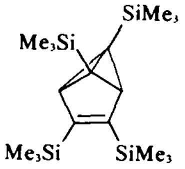

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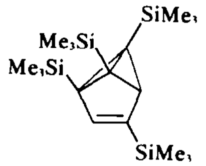

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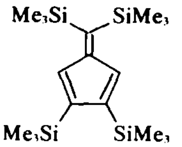
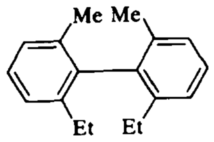
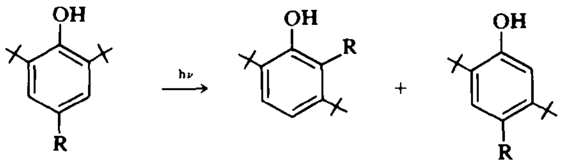


58



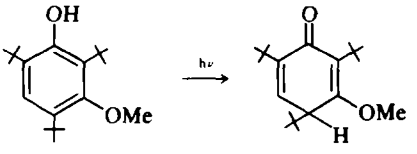
59



60 **61** **62**

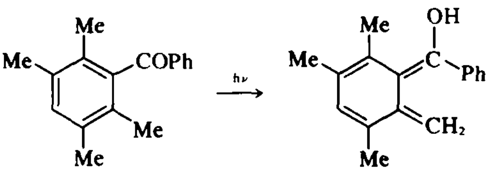
R = H, Me, OMe, t-Bu, and OH.

In comparison with these examples of photoketonisation, aryl ketones undergo photoenolisation to produce *o*-quinodimethanes which in turn may be trapped by dienophiles such as maleic anhydride.[100] The conversion of **65** into **66** provides an example: the systems are photochromic.



64 **63**

Deuterium labelling studies have indicated that an *o*-quinodimethane (**67**) is probably formed as an intermediate in the photoisomerisation of 1,2-dihydronaphthalene (**68**) to the cyclopropane (**69**).[101] The related transformation **70**→**71** also probably involves the formation of an intermediate *o*-quinodimethane (**72**) followed by a photochemical 1,7-sigmatropic H-shift.[102]



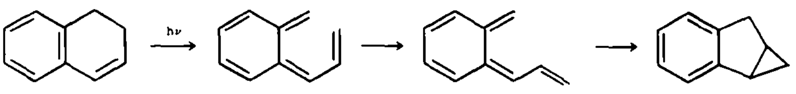
65 **66**

shown that tri- and tetra-t-butylnaphthalenes undergo photochemical 1,4-bonding in one ring to give the corresponding "Dewar" isomers.[105]

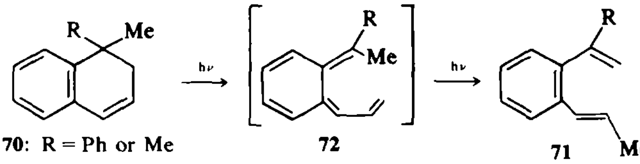
Photoisomerisation of ionic species. In view of the 1,3-bonding which is proposed to occur in S_1 benzene to give the prefulvene diradical (Fig. 5) as a precursor of benzvalene and fulvene, it is interesting that an analogous process occurs on excitation of the hexamethylbenzenonium ion (**73**) to give the bicyclic isomeric carbonium ion (**74**).[106] The tetramethylbenzenonium ion (**75**) formed from durene and fluorosulphonic acid at −90° undergoes a similar photoisomerisation to **76**.[107] In order to explain some of the reactions which occur on irradiation of benzene under acid conditions, it had earlier been proposed that this type of process may occur in the parent benzenonium ion;[108] but an alternative mechanism involving protonation of benzvalene is now known to be more important.[109]

Irradiation of tropylium fluoroborate in 5% aqueous sulphuric acid gives the alcohol (**77**) and the ether (**78**), probably via the isomeric carbonium ion (**79**).[110]

We refer in conclusion to a most interesting recent proposal by Barltrop and Day that analysis of reactions which involve the transposition of atoms in 6-membered aromatic rings can be analysed in terms of the set of twelve permutation patterns shown in Fig. 14, rather than by way of the benzvalene, Dewar-benzene, or prismane intermediates which, as they correctly point out, have been more often proposed than established.[111,112]



68 **67** **69**

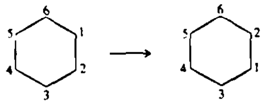


70: R = Ph or Me **72** **71**

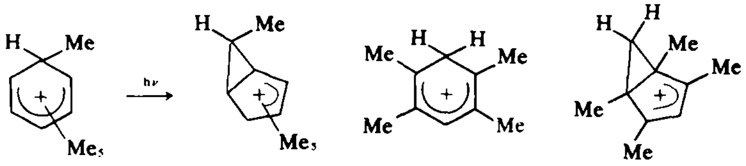
The photoisomerisation of indenes to isoindenes is related to the first stage of the foregoing transformations.[103]

It is interesting that naphthalene and higher condensed polycyclic aromatic systems are in general much less photolabile than benzene. Naphthalene itself does not apparently undergo photoisomerisation to fulvene, benzvalene, or Dewar-derivatives, and even the more generally reactive azulene only undergoes a highly inefficient $(\Phi \leq 10^{-5})$ irreversible photoisomerisation to naphthalene.[104] Mandella and Franck have however

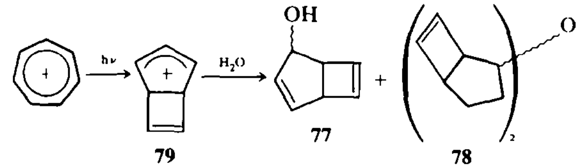
Their approach is essentially to concentrate on the pattern of transposition rather than speculate on the "innumerable" chemical intermediates that are conceivable. Thus the transposition



would be classified as of type P_2 in Fig. 14 (compare pathway *a* in Fig. 13). It remains to be seen to what extent



73 **74** **75** **76**



79 **77** **78**

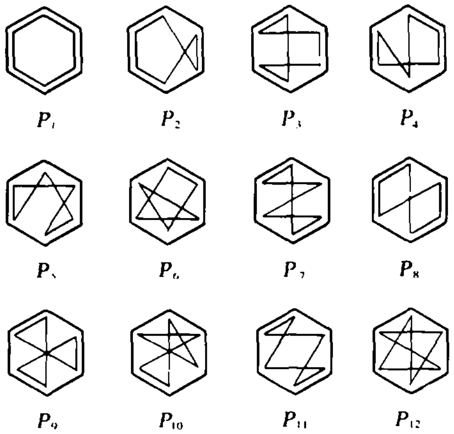


Fig. 14.

chemists will find this new notation a convenient alternative, as distinct from adjunct, to the more conventional type of analysis depicted in Fig. 13. However, the authors in their enthusiasm for the new notation may have tended to overestimate the degree of uncertainty which now exists concerning the mechanisms of ring transposition processes (see Ref. 113). This new approach may be useful in stimulating attempts to discover ring transposition processes which do not fit into the normal pattern of valence-bond intermediates; but the fact remains that no such exceptions are yet apparently known.

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