PHOTOADDITION TO THE BENZENE RING

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ABSTRACT

Concerted cycloadditions of ethylene and buta-1,3-diene to benzene are analysed by an orbital symmetry procedure which shows that the orbital degeneracy in benzene renders the Woodward–Hoffmann rules inapplicable to reactions proceeding via electronically excited states. Various experimental findings are surveyed in the light of this analysis. In reactions between species differing significantly in ionization potential, there is evidence that polar factors may be important, and novel acid–catalysis effects have been observed.

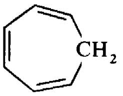
Some 1,2-, 1,3- and 1,4-additions of various amines to benzene are described. These require the presence of a proton donor, and are of synthetic utility. An example of intramolecular 2,5-addition of a t-amine is reported, and offers promise of a simple approach to some hitherto inaccessible ring systems.

INTRODUCTION

The benzene ring may participate in three main types of photochemical reaction, as follows.

(i) Addition of photochemically generated carbenes, free radicals and the like. The benzene ring is not itself photoexcited. Examples of such reactions are:

(a) $CH_2N_2 \xrightarrow{h\nu} CH_2 + N_2 \xrightarrow{C_6H_6}$



(b) $ArI \xrightarrow{h\nu} Ar\cdot + I\cdot \xrightarrow{C_6H_6} C_6H_5Ar$

(c) $Cl_2 \rightarrow 2Cl\cdot \xrightarrow{C_6H_6} C_6H_6Cl_6$

(ii) Reaction of ground state benzene with photoexcited species, e.g. the photoaddition of maleimide to benzene.

(iii) Reactions in which the benzene ring is (a) excited, or (b) undergoes photochemical charge transfer. Examples of type (a) include photoisomerizations to fulvene, benzvalene, Dewar-benzene etc., and the photoaddition of simple mono-olefins and 1,3-dienes, whereas type (b) is illustrated by the photoaddition of maleic anhydride (benzene donor) and amines (benzene acceptor) to benzene.

One should also bear in mind that energy transfer may occur from excited singlet or triplet benzene to other species, as in the benzene-photosensitized *cis–trans* isomerization of olefins.

This paper will be concerned with photoaddition processes in categories (ii) and (iii). Some of these, but not all, are cycloadditions.

ORBITAL SYMMETRY FACTORS

The course of concerted cycloadditions to benzene is governed by orbital symmetry considerations, just as with cycloadditions involving only aliphatic systems. However, the celebrated Woodward–Hoffmann rules were based on the symmetry properties of aliphatic systems, and cannot be applied to predict the course of photoreactions involving the benzene ring. The reason for this lies in the orbital degeneracy of ψ_2 and ψ_3 and ψ_4 and ψ_5 in benzene, and the fact that excitation of benzene ($S_0 \rightarrow S_1$, S_2 etc) may be analysed in terms of more than one orbital transition. Thus for the S_1 state of benzene (${}^1B_{2u}$) we have transition densities equivalent to $\psi_2\psi_5 - \psi_3\psi_4$, and for the S_2 state (${}^1B_{1u}$), $\psi_2\psi_4 + \psi_3\psi_5$. So each of these excited states has two orbital components, either of which can serve to establish a valid correlation with an excited state of a reaction product in an orbital level diagram. It is this duality which makes the Woodward–Hoffmann rules inapplicable in benzene photochemistry. As an example, we may compare the suprafacial/suprafacial 1,2-addition of ethylene to benzene (*ss*) with the corresponding suprafacial/antarafacial process (*sa*).

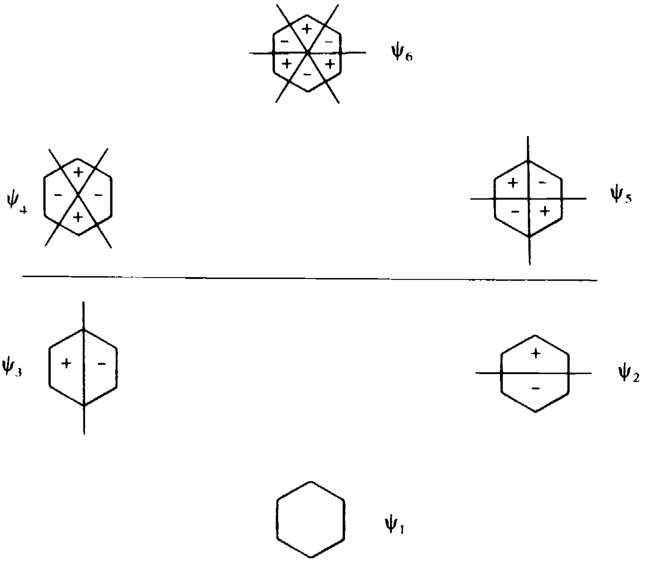
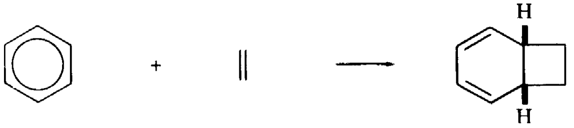


Figure 1. Molecular orbitals of benzene

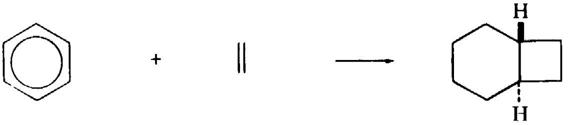
Figures 2 and *3* show the correlation diagrams for these two cases[†].

[†] Correlations for photoreactions of benzene (other than those giving diradical species) are made with the lowest electronic excited state of the non-aromatic products following normal practice. But there is generally no experimental evidence that an excited state of the product is actually formed, i.e. that the process is adiabatic, and there may well be partial or total relaxation into the electronic ground state of the product at some intermediate point along the reaction coordinate.

(ss)



(sa)



Note that non-Hückel levels are used for ethylene in acknowledgement of the fact that S_1 (ethylene) > S_1 (benzene). It will be seen that in each case, S_1 of the product (π'_2 and π'_3 each singly occupied) correlates only with S_0 (ethylene) + S_2 (benzene) ($^1B_{1u}$); in the *ss* case, correlation is through the $\psi_3\psi_5$ component of this state, and in the *sa* case through the $\psi_2\psi_4$ component. Thus we have a situation where *ss* and *sa* modes of concerted cycloaddition are equally allowed, contrary to predictions based on the Woodward–Hoffmann rules. The 1,2-photoaddition of ethylene to benzene could in principle be non-stereospecific, yet fully concerted; but steric and

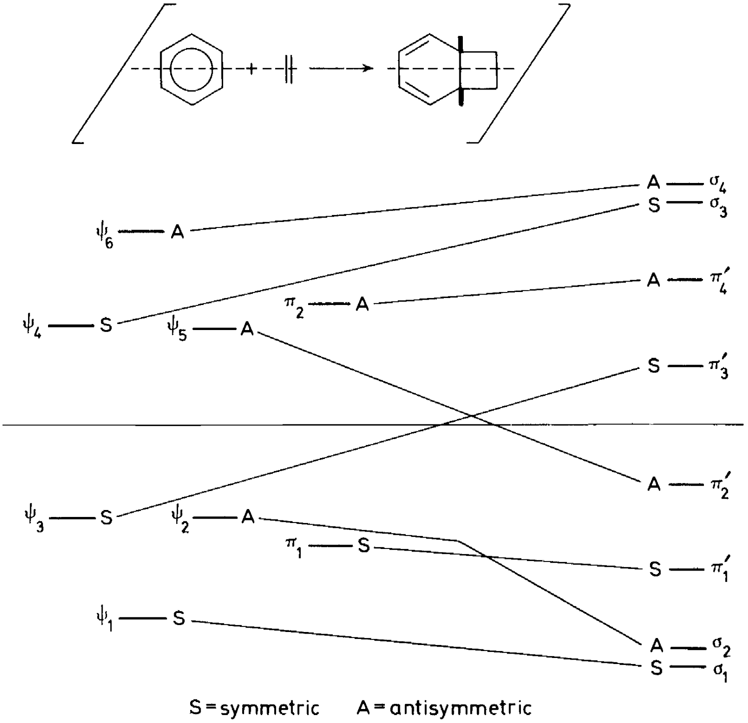


Figure 2

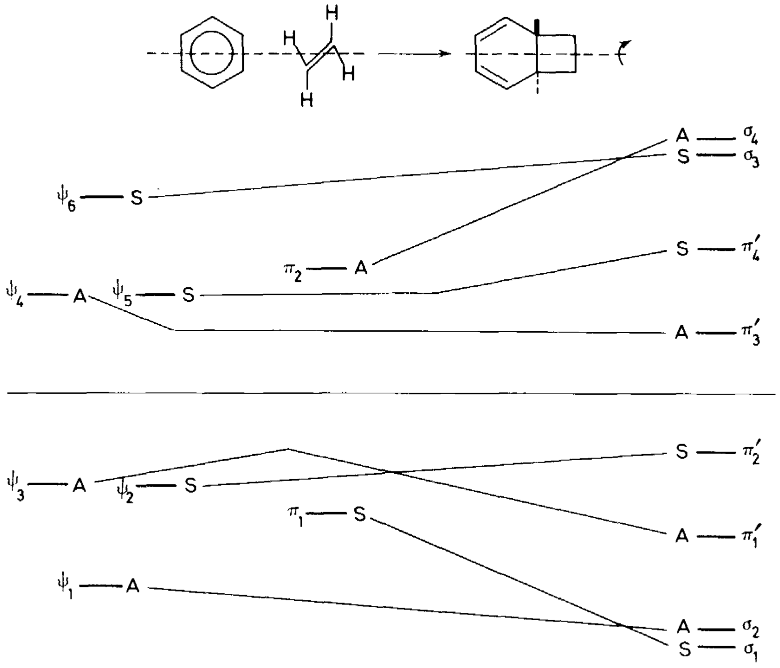


Figure 3

strain factors would be expected to favour the *ss* process in practice. It should also be noted that the S_1 (benzene) + S_0 (ethylene) concerted process is symmetry forbidden in each case, but that the *sa* process is allowed by the thermal pathway. In the case where S_1 (benzene) > S_1 (ethylene), one may for purposes of constructing a level correlation diagram put the energy of the π_1 level above that of the ψ_2, ψ_3 levels, and likewise place π_2 below ψ_4, ψ_5. It may readily be shown that the 1,2-additions can now occur in a concerted manner by reaction of S_0 (benzene) with S_1 (ethylene). This state of affairs is realized in practice when the ethylene bears substituents which reduce the level of its S_1 state below that of S_1 (benzene), as with maleimide, for example.

The results of a more extensive analysis of concerted cycloadditions to benzene are given in ref. 1. They indicate that concerted 1,2- and 1,4- *ss* cycloadditions of simple ethylenes to benzene are symmetry forbidden if they involve S_0 (ethylene) and S_1 (benzene) (as they normally would), but that 1,3-cycloaddition, i.e. *meta*-addition, is allowed. Moreover, the 'allowedness' of this rather remarkable process is insensitive to the mechanistic details: bond 1 may be formed prior to bonds 2 and 3 (*Figure 4*), or subsequently (*Figure 5*), or all three may be formed synchronously. The stereospecificity and the insensitivity to proton-donors and solvent polarity

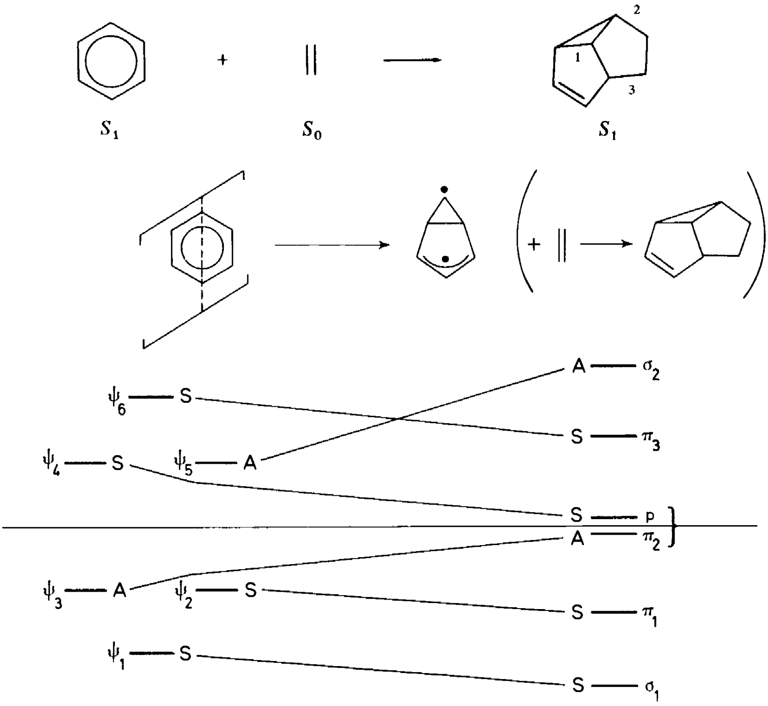


Figure 4. 1,3-Bonding in benzene

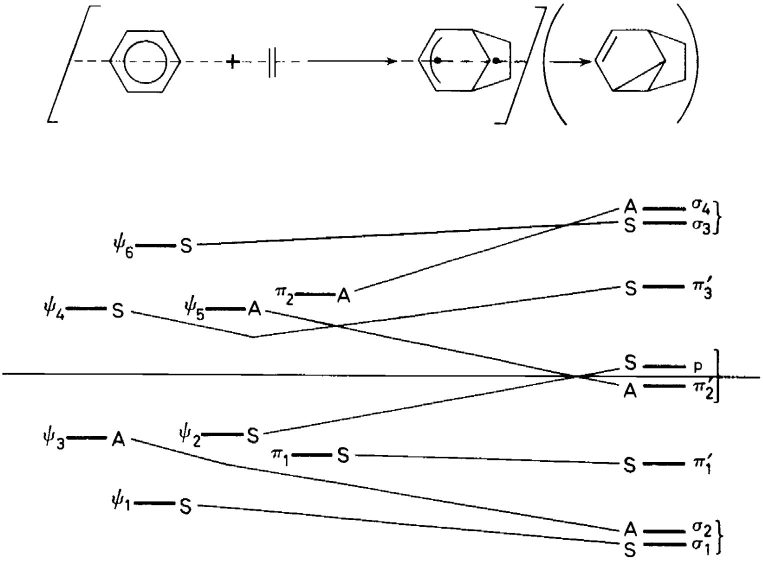
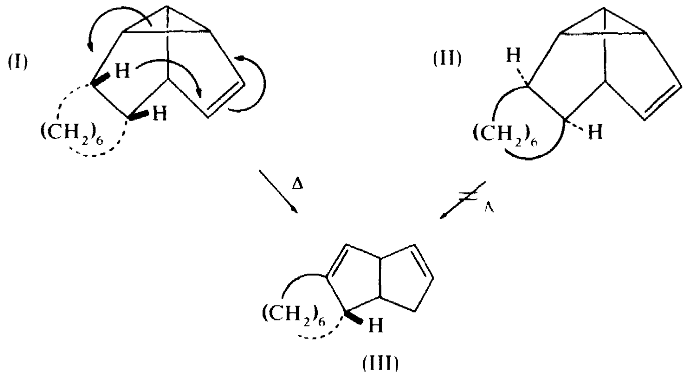


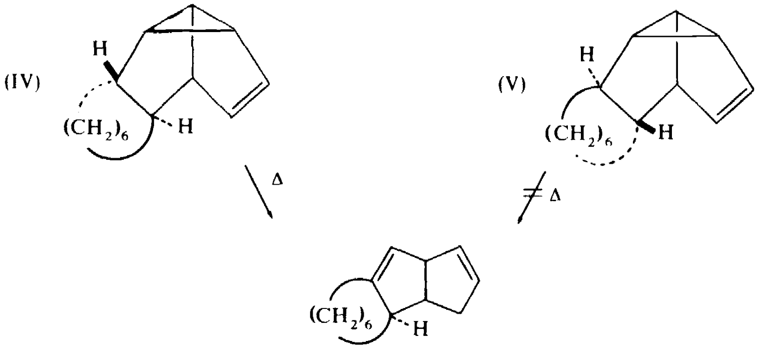
Figure 5. 1,3-Addition of ethylene to benzene

indicate that bonds 2 and 3 at least are formed in a substantially concerted manner.

The results of this analysis do much to explain why 1,3-cycloaddition is the predominant mode to be observed experimentally with simple olefins and benzene. This reaction was discovered independently in 1966 by Wilzbach and Kaplan[2] and by Bryce-Smith, Gilbert and Orger[3], and appears to be completely stereospecific with respect to the olefin. Thus the addition of S_0 *cis*-cyclo-octene to S_1 (benzene) gives two main 1 :1 adducts, (I) and (II) in the ratio ca. 1 :5.



The minor adduct (I) undergoes thermal isomerization to the diene (III), a process which may readily be rationalized in terms of a symmetry-allowed suprafacial 1,5-sigmatropic H-shift. Such a process is sterically impossible with isomer (II).



In like manner, *trans*-cyclo-octene gives the two isomeric 1,3-adducts (IV) and (V) in approximately equal amounts, of which only (IV) undergoes a thermal 1,5-sigmatropic shift. Prolonged irradiation of benzene-cyclo-octene mixtures leads to significant benzene-sensitized *cis–trans* isomerization of the olefin, so from each geometric isomer, the other is slowly formed and thence also its corresponding benzene adducts. Thus the addition *appears* to become non-stereospecific on prolonged irradiation, but is not really so.

The quantum yields for 1,3-additions of the cyclo-octenes to benzene tend to increase with increasing olefin concentration, and are ca. 0.5 at a 9:1 olefin/benzene ratio. Thus many reactions of this type are remarkably efficient, and of definite preparative value. Adducts may readily be prepared in quantities of the order 10 to 50 g per run. But the quantum yield for 1,3-addition varies from olefin to olefin, and with cyclohexene for example is ca. 0.01. At low concentrations of olefin, telomers of benzene are formed in which values of n up to ca. 25 have been observed[4]: see *Figure 6.*

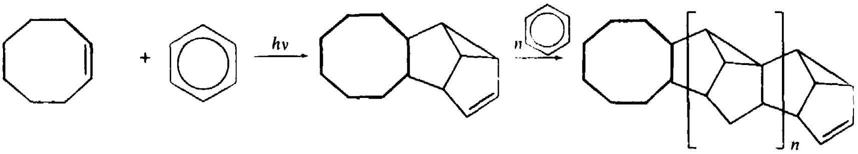
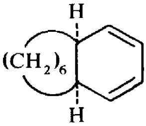
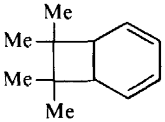


Figure 6. Phototelomerization of benzene

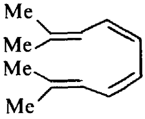
It was until recently believed that 1,3-addition of mono-olefins to benzene occurs almost exclusively. But it has now been observed both at Reading[5] and by Wilzbach and Kaplan[6] in the USA that stereospecific 1,2-addition of some mono-olefins to benzene can be an important process in the early stages of reaction. The initial 1,2-adducts, e.g. (VI) and (VII) from *cis*-cyclo-octene and tetramethylethylene respectively, rapidly build up to a low stationary concentration and may even predominate in the products at low conversion; but they normally only constitute a very low proportion of the products from normal preparative runs because they are readily photo-dissociated through absorption of radiation at ca. 270–290 nm, i.e. beyond the benzene absorption front. For this reason, they are normally observed only if a low-pressure mercury lamp is used (which has very little emission in the 270–290 nm region), rather than a medium-pressure lamp. Indeed, no trace of these photo-labile 1,2-adducts can usually be found if a medium-pressure lamp is employed. The ratio of 1,2- to 1,3-adducts generally decreases with increased time of irradiation, for the 1,3-adducts are photostable. The 1,2-photoadducts may be conveniently isolated in the form of their thermal adducts with dienophiles, for example the 1:1:1 adduct (IX), m.pt 227°, from *cis*-cyclo-octene, benzene, and *N*-phenylmaleimide. The C_8 ring is probably *cis*-fused, for *cis*- and *trans*-cyclo-octene give chemically distinct



(VI)

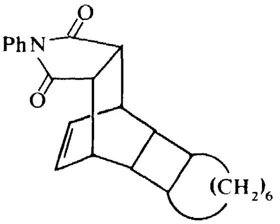


(VII)

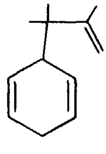


(VIII)

single 1,2-adducts with benzene in what may reasonably be concluded to be stereospecific reactions. Irradiation of the 1,2-adduct (VII) through Pyrex ($\lambda > 290$ nm) leads mostly to its dissociation to tetramethylethylene and benzene, but a small amount of the tetraene (VIII) appears also to be formed, as judged by the appearance of new absorption maxima at 288, 303 and 320 nm. In the addition of tetramethylethylene to benzene, the main product is in fact a 1,4-adduct (X) formed by a type of photochemical 'ene-addition': the ratios of 1,4-, 1,3- and 1,2-adducts are 8:4:1 respectively after six hours irradiation at 254 nm with a 6W low pressure Hg lamp[7]. (Stereospecific 1,4-cycloaddition of certain mono-olefins to benzene has been reported recently by Wilzbach and Kaplan[6] to occur with low quantum efficiency [$\Psi \sim 0.01$–0.02 with the but-2-enes], and Srinivasan[8] has observed 1,4-cycloaddition of cyclobutene to benzene. Foulger[9] has established that this latter process occurs stereospecifically.)



(IX)



(X)

The following important question arises. How is it that stereospecific 1,2- and 1,4-photochemical cycloadditions of mono-olefins to benzene can occur under conditions which appear to involve S_1 (benzene) ($^1B_{2u}$) and S_0 (olefin) when concerted 1,2- and 1,4-additions of S_0 olefin to S_1 benzene are forbidden on orbital symmetry grounds? There is at present insufficient information concerning the 1,4-cycloadditions to permit mechanistic discussions (although strain is obviously an important factor in the 1,4-cycloaddition of cyclobutene to benzene), but for the seemingly anomalous 1,2-cycloadditions, and the 1,4-'ene-additions' there is evidence that *polar* factors are important. Thus in the photoadditions of *cis*- and *trans*-cyclo-octenes to benzene, the quantum yields for 1,3-addition are closely similar

Table 1. Quantum yields (Ψ) for 1,2- and 1,3-cycloadditions of *cis*-cyclo-octene to benzene (solvent iso-octane) at 20° and 254 nm

Process	Olefin 6.9M Benzene 1.1M	Olefin 3.8M Benzene 1.1M	Olefin 3.0M Benzene 1.1M + EtOH 7.0M
Ψ for 1,2-adduct	0.14–0.15	0.10	0.10
Ψ for 1,3-adduct (II)	0.41–0.50	0.34	0.37
Ψ for 1,3-adduct (I)	0.04–0.05	0.05	0.02
Ψ (II) + Ψ (I)	0.45–0.55	0.39	0.39
Ψ (total adducts)	0.65 ± 0.05	0.49	0.49
$\Psi_{1,2}/\Psi_{1,3}$	0.29 ± 0.04	0.26	0.26

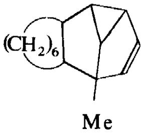
Table 2. Quantum yields (Ψ) for 1,2- and 1,3-cycloadditions of *trans*-cyclo-octene to benzene (solvent iso-octane) at 20° and 254 nm

Process	Olefin 3.8M Benzene 1.1M	Olefin 1.5M Benzene 1.1M
Ψ for 1,2-adduct	0.39 ± 0.01	0.35
Ψ for 1,3-adduct (V)	0.16	0.13
Ψ for 1,3-adduct (IV)	0.16	0.14
Ψ (V) + Ψ (IV)	0.32	0.27
Ψ (total adducts)	0.72 ± 0.01	0.62
$\Psi_{1,2}/\Psi_{1,3}$	1.2	1.3

(The effect of ethanol on the addition of *trans*-cyclo-octene is currently under investigation.)

for the two olefins, but the quantum yield for 1,2-addition is much higher for the *trans*-olefin, as shown by results obtained by Miss Hilary Tyrrell, and listed in *Tables 1* and *2*.

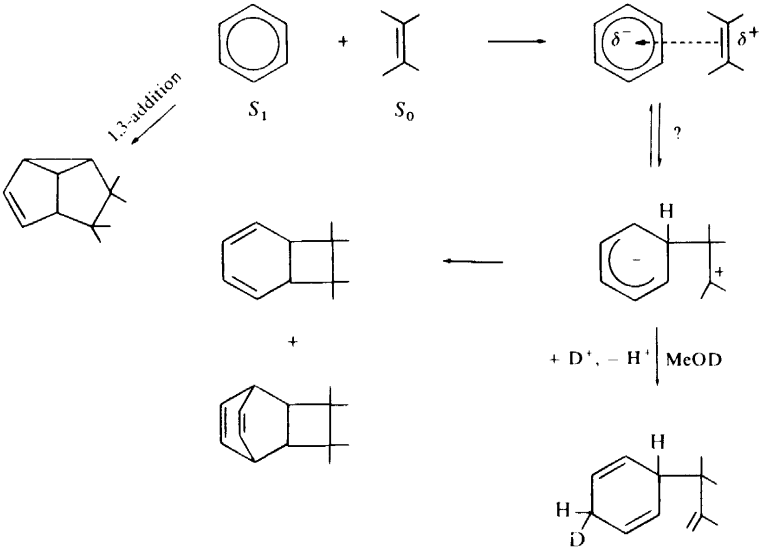
Of these two olefins, *trans*-cyclo-octene is the stronger electron donor (the first ionization potentials are 8.56 and 8.81 eV for the *trans*- and *cis*-isomers respectively), and has the greater tendency to undergo 1,2-cycloaddition to benzene. In passing from benzene to the weaker acceptor toluene, the tendency for 1,2-addition virtually disappears, and only 1,3-adducts of type (XI) have been detected. It will be seen from *Table 1* that the 1,2- and 1,3- modes of addition of *cis*-cyclo-octene to benzene are relatively insensitive to the polarity of the medium. But this is not so when the olefin is tetramethylethylene. It has been found with this olefin that the 1,2-cycloaddition and the 1,4-'ene-addition' to benzene are markedly promoted by the presence of methanol, although methanol has no effect on the 1,3-addition. The use of acetonitrile as solvent enhanced the initial rate of 1,2-addition by a factor of ca. 2, although it has no effect on either the 1,3- or the 1,4-addition processes. The most convincing evidence for the involvement of a polar intermediate appears to come from the observation that the use of MeOD as solvent leads to the incorporation of deuterium in the 4-position of the benzene-derived moiety in the 'ene-adduct' (X). Moreover, the use of hexadeuteriobenzene in place of ordinary benzene (methanol absent) led to the incorporation of protium (H) in the 4-position substantially non-stereospecifically: ref. 7 gives further details. Again, this result indicates that the 'ene-addition' of tetramethylethylene to benzene does not occur to any marked extent by a concerted mechanism involving a cyclic intermediate, contrary to what might have been expected *a priori*.



(XI)

Preliminary studies by R. Forrester indicate that the tendency for 1,4-'ene-addition' to benzene is much less marked with trimethylethylene than with the stronger donor tetramethylethylene, and indeed, no 'ene-addition' appears to have been detected with *cis*- and *trans*-but-2-enes[6].

Thus, although studies are incomplete, there seems to be evidence that the 1,4-'ene-addition' and perhaps also the 1,2-cycloaddition are derived from an intermediate or intermediates having a degree of polar character, but that 1,3-cycloaddition does not involve polarity factors to any significant extent. An explanation consistent with these findings is that 1,3-addition occurs via the concerted or part-concerted routes from S_1 (benzene) plus S_0 (olefin), as already discussed, but that the 1,4-'ene-addition' and the 1,2-cycloaddition occur via a polarized intermediate formed by a degree of electron transfer from donor S_0 (olefin) to acceptor S_1 (benzene). This intermediate could be an exciplex species of the type discussed by Morrison and Ferree[10], or could even be represented as (or in equilibrium with) a zwitterion (XII), which would of course tend to be stabilized to some extent by polar and proton-donor solvents, depending on its lifetime. Thus we may represent the case of tetramethylethylene and benzene as follows.



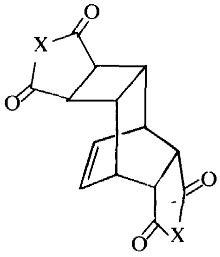
(XII)

Stereospecificity in 1,2- and 1,4-cycloaddition by this route would be governed not by concertedness in the usual sense, but rather by coulombic interaction between the charged centres.

It is envisaged that the charge-transfer process will be favoured relative to the competitive 1,3-addition (i) by substituents which increase the donor strength of the olefin and increase the acceptor character of the benzene, and (ii) by factors which can stabilize the intermediate dipoles.

MALEIMIDE AND MALEIC ANHYDRIDE AS ADDENDS TO BENZENE

In contrast with the olefins discussed above, these two ethylenic addends have strong electron-acceptor properties. They are isoelectronic, and give chemically similar 2:1 photoadducts (XIII*a* and *b*) with benzene. Yet surprisingly, the mechanisms for formation of these two adducts are markedly different.

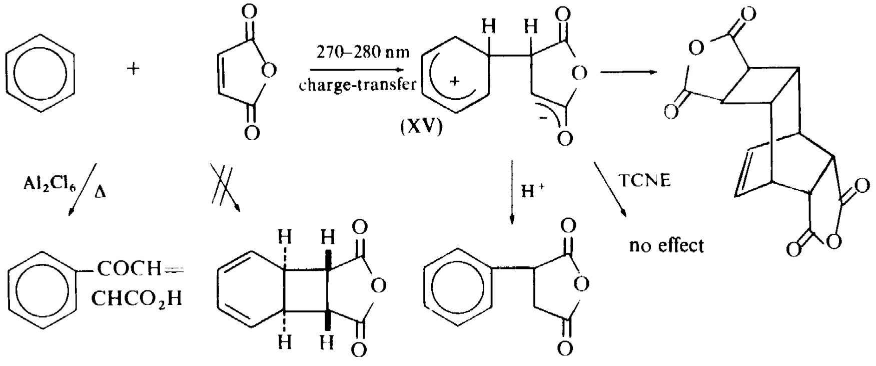


(XIII: *a*, X = O; *b*, X = NH)

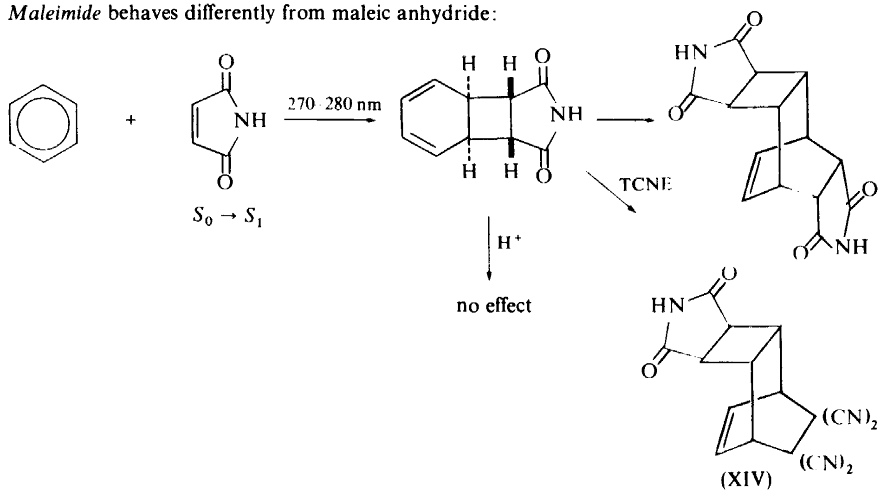
The photoaddition of maleimide undoubtedly proceeds by way of 1,2-photoaddition of S_1 (maleimide) to S_0 (benzene), for S_1 (maleimide) lies below S_1 (benzene). As mentioned earlier, this is allowed as a concerted process. Moreover, solutions of maleimide in benzene show no charge-transfer absorption extending beyond the benzene solvent from at ca. 270 nm (contrast maleic anhydride), although Dr M. A. Hems has shown[11] by examination of ultrathin films of such solutions that anomalously strong absorption, reasonably attributable to charge-transfer excitation, occurs in the 240–260 nm region. In accordance with this, the photoaddition process proves to be insensitive to the presence of proton-donors such as trifluoroacetic acid or methanol[12], but sensitive to the presence of tetracyanoethylene: this strong dienophile intercepts the intermediate 1,2-adduct as the 1:1:1 adduct (XIV).

In contrast, solutions of maleic anhydride in benzene show strong charge-transfer absorption extending beyond the benzene solvent front, and substantially swamping the very weak $S_0 \rightarrow S_1$ absorption of free maleic anhydride[13]. Thus, the photoaddition in this case proceeds by way of charge-transfer excitation to give a polarized intermediate [depicted below as a zwitterion (XV)] in which benzene is the donor (contrast the case of tetramethylethylene above where benzene is the acceptor). This intermediate is insensitive to tetracyanoethylene, which is a much weaker nucleophile than maleic anhydride, but can be intercepted by a proton-donor such as trifluoroacetic acid or methanol to give phenylsuccinic anhydride. The formation of this anhydride constitutes an example of *photoelectrophilic substitution*; one may note the resemblance between the structure of the proposed zwitterionic intermediate(XV) and that of the classical Wheland intermediate in conventional electrophilic aromatic substitution processes. *Figure* 7 summarizes these results.

Addition of the second molecule of maleic anhydride to the polarized intermediate (XV) could be a concerted thermal process, but it is obviously



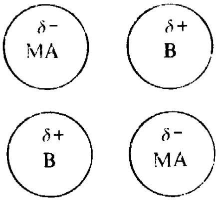
Maleimide behaves differently from maleic anhydride:



The maleimide-benzene charge-transfer absorption occurs at ca. 240–260 nm and is normally swamped by the strong benzene absorption in this region.

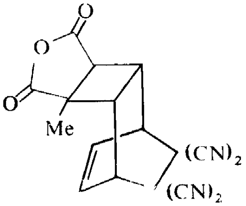
Figure 7. Photoaddition of maleic anhydride to benzene: effect of proton donors

very efficient and requires the maleic anhydride to function as a nucleophile —an unusual role, but one for which precedents exist[14]. However, if the reaction is carried out in the presence of *cis*-cyclo-octene, which must be a stronger nucleophile than maleic anhydride, no adduct incorporating the olefin appears to be formed[15]. A possible explanation for this apparent anomaly may lie in the polarized character of the weak ground state 1:1 complex between maleic anhydride and benzene, $MA^{\delta-}$ ------ $B^{\delta+}$. Although the precise degree of charge-transfer in the ground state of such a complex is uncertain, a small dipole moment should lead to dipole association in a non-polar hydrocarbon medium. We may diagrammatically represent a 2:2 cluster as follows:

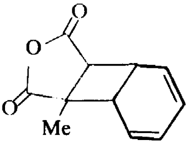


From this it may be seen that a complexed benzene molecule has at least two adjacent maleic anhydride molecules. These are better situated to undergo addition than, say, an olefin which is not effectively participating in the complex equilibria. In short, the efficiency of the addition of the second molecule of maleic anhydride may be largely determined by entropy factors.

The picture is completed when we consider methylmaleic anhydride. The methyl group renders this a weaker electron-acceptor than maleic anhydride, so that no charge-transfer absorption is apparent in the spectrum of its solution in benzene. Thus the lowest energy excitation involves 'free' methylmaleic anhydride, as with maleimide, and the formation of a 1,2-adduct (XVI) by a symmetry-allowed concerted process. But methylmaleic anhydride is too weak a dienophile to intercept this intermediate, so no 2:1 adduct is obtained, and only a low photostationary concentration of (XVII) results, as with the analogous 1,2-addition of simple olefins mentioned above. But irradiation in the presence of tetracyanoethylene, or addition of tetracyanoethylene to the solution after irradiation, leads to the 1:1:1 adduct (XVI)[16]. As expected, proton-donors such as trifluoroacetic acid have no effect on the irradiated methylmaleic anhydride–benzene system. The use of dimethylmaleic anhydride in place of the monomethyl derivative leads to precisely analogous results[16].



(XVI)

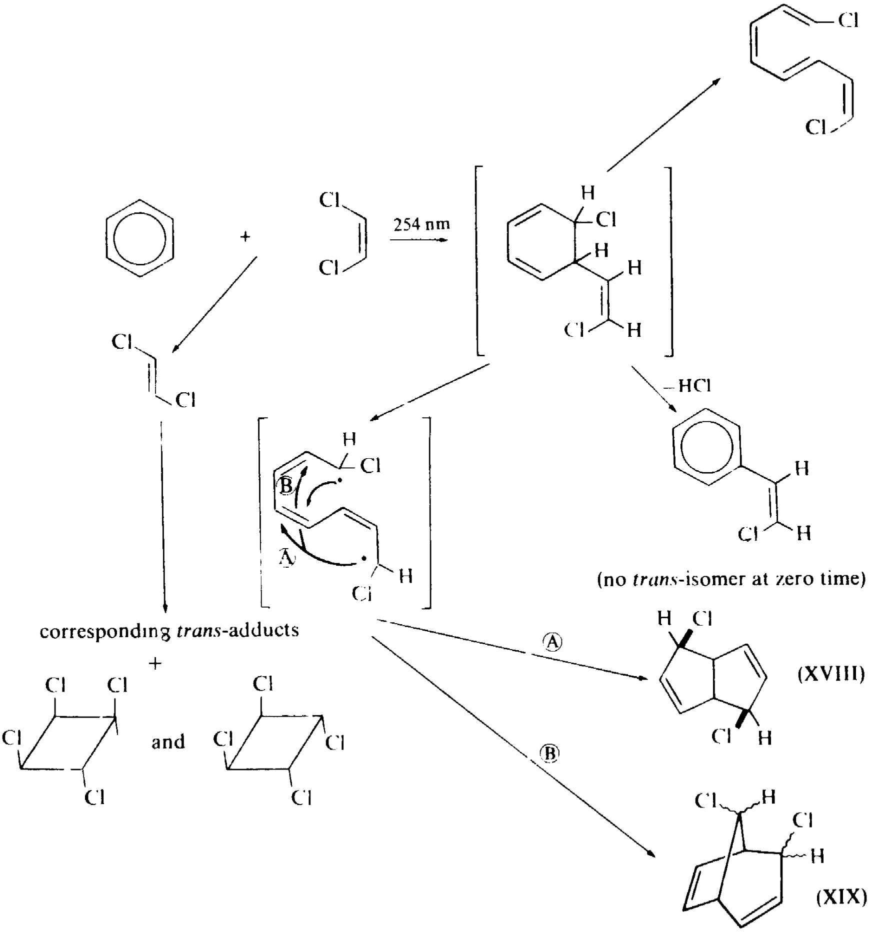


(XVII)

It may be noted in passing that the bis-anhydride (XIII*a*) reacts with diamines to give structurally interesting polymers of the polyimide type. It could if necessary be prepared on a large scale using benzophenone as sensitizer and sunlight as the radiation source.

PHOTOADDITION OF *CIS*-1,2-DICHLOROETHYLENE TO BENZENE

This system has been carefully studied by Dr B. E. Foulger[17]. The main initial product is *cis*-β-chlorostyrene, formed stereospecifically (a finding which almost certainly rules out the intermediacy of free 2-chlorovinyl radicals), but the *trans*-isomer soon appears, together with *trans*-1,2-dichloroethylene, evidently through benzene-sensitized *cis–trans* photoisomerization. Other products include a 1,8-dichloro-octatetraene, previously reported by Simons[18], tetrachlorocyclobutanes, and two decidedly unusual bicyclic 1:1 adducts (XVIII) and (XIX). The formation of these may be rationalized in terms of an initial acyclic 1,2-addition of C—Cl to benzene, as shown in *Scheme 1*.

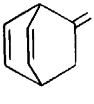


Scheme 1. Photoreactions of *cis*-1,2-dichloroethylene with benzene

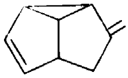
PHOTOREACTIONS OF DIENES WITH BENZENE

(a) 1,2-Dienes

Irradiation of a two per cent solution of allene in benzene under nitrogen at 254 nm gives the 1,4-adduct (XX) and 1,3-adduct (XXI) in a ratio of ca. 2:1, together with traces of two other 1:1 adducts, as yet unidentified. Cyclonona-1,2-diene likewise gives 1,4- and 1,3-adducts in the ratio 4:1[19].



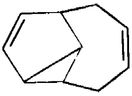
(XX)



(XXI)

(b) 1,3-Dienes

Figure 8 gives the orbital correlation diagrams for the *para*-1,4-concerted *ss* cycloadditions of *cisoid* and *transoid* buta-1,3-diene to benzene. For the *cisoid* conformer the process is forbidden through S_0 (diene) + S_1 (benzene) (the excitation situation which obtains in normal practice) whereas that for the *transoid* conformer is allowed. It is therefore most gratifying that Kraft and Koltzenburg[20] have found that 1,3-dienes do indeed react with S_1 (benzene) to give initially the strained product derived from the *transoid* conformer rather than the comparatively unstrained isomeric adduct from the *cisoid* conformer. The symmetry axis for addition of the *transoid* conformer does not pass through any of the C—C bonds in benzene, so it may well be that the energy difference between 'allowed' and 'forbidden' processes in this system is smaller than for the corresponding additions of *cisoid* butadiene. It may be predicted from a similar orbital symmetry analysis[1] that S_0 (*cisoid* buta-1,3-diene) could undergo concerted *ss meta* addition to S_1 (benzene), giving adduct (XXII), but this process has not yet been observed.



(XXII)

PHOTOREACTIONS OF BENZENE AND AMINES

(*a*) Tertiary amines such as triethylamine have been found greatly to promote the benzene-sensitized *cis–trans* isomerization of olefins in the liquid phase. Thus the rate of formation of *trans*- from *cis*-cyclo-octene in benzene under nitrogen could be increased about tenfold in the presence of triethylamine. In contrast, methanol had no appreciable effect. The process is of preparative interest, for five to ten per cent solutions of *trans*- in *cis*-cyclo-octene may readily be built up[21]. The mechanism is currently under investigation.

(*b*) *Photoaddition of amines to benzene*—This reaction was first reported in 1967[22], and has since proved to be very general in scope[23]. The main products are 1:1 photoadducts formed by 1,4-addition to the benzene ring, but in some cases minor quantities of products formally arising from 1,2- and 1,3-addition are also obtained. The presence of a proton-donor is required: primary and secondary amines can themselves function in this capacity, but tertiary amines require the addition of a separate proton source such as methanol or water. The mechanism is evidently related to that of the Birch reduction, and indeed small quantities of cyclohexa-1,4-diene and the tetrahydrobiphenyl (XXIII) are also formed together with dehydrodimers of the amine. A key step in the thermal Birch reduction of benzene is electron transfer to benzene via ammonia-solvated electrons to form the

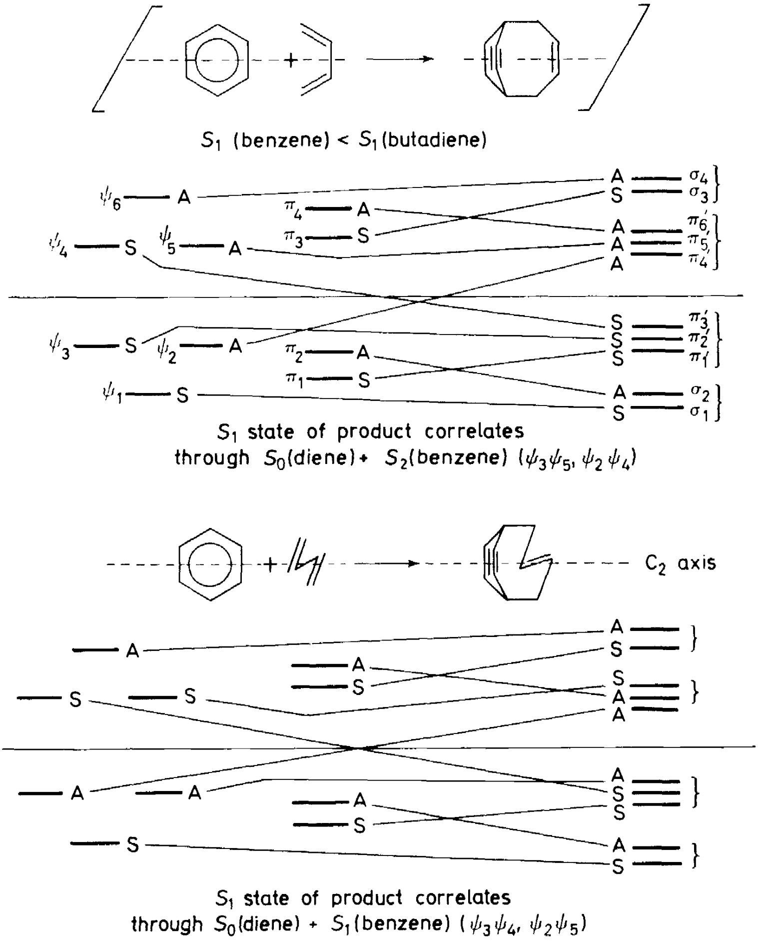
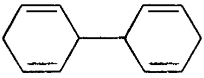


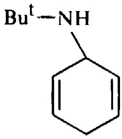
Figure 8. Photoadditions of butadiene to benzene

benzene radical-anion. Amines are not sufficiently strong donors to react analogously in the ground state, but they can do so when benzene is excited to the S_1 state (in which it is able to accept an electron into the bonding orbitals ψ_2 and ψ_3): amines strongly quench the fluorescence of benzene.

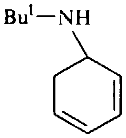
The primary amine *t*-butylamine gives mainly the 1,4-adduct (XXIV), with smaller proportions of the 1,2-adduct (XXV) and the 1,3-adduct (XXVI) having λ_{max} 223 nm. Methanol has no effect on the course or rate of the reaction. Adduct (XXVI) is evidently not a primary photoproduct, for it can be formed by irradiation of the separated 1,2-adduct (XXV) in benzene, via hexatriene (XXVII), λ_{max} 339 nm, which has also been isolated, but which is very photolabile, being converted into the isomer (XXVI) even on exposure to daylight.



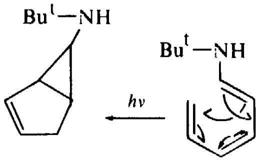
(XXIII)



(XXIV)

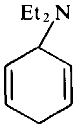


(XXV)

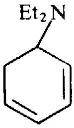


(XXVI) (XXVII)

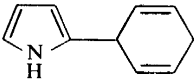
The secondary amine diethylamine gives mainly the 1,4-adduct (XXVIII) together with a minor proportion of the 1,2-adduct (XXIX). Methanol only promotes these additions to a slight extent, if at all. Other secondary amines behave similarly, but pyrrole gives the α-derivative (XXX). The use of hexadeuteriobenzene showed that the addition of pyrrole is not stereospecific, the ratio of *cis*- to *trans*-adducts being ca. 3:2[23].



(XXVIII)

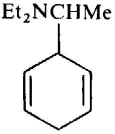


(XXIX)

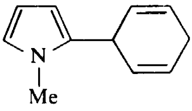


(XXX)

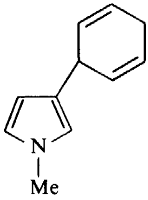
Tertiary amines react at the α-positions; thus triethylamine gives the 1,4-adduct (XXI). Negligible quantities are formed unless a proton-donor such as methanol is present: acetonitrile which is similarly polar, but a poor proton-donor, is without effect. Manning[21] has observed that *N*-methylpyrrole undergoes substitutive addition at both the α- and β-positions when irradiated with benzene in methanol, giving the adducts (XXXII), (XXXIII) and (XXXIV) in the approximate ratio 2:1:1 respectively.



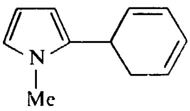
(XXXI)



(XXXII)



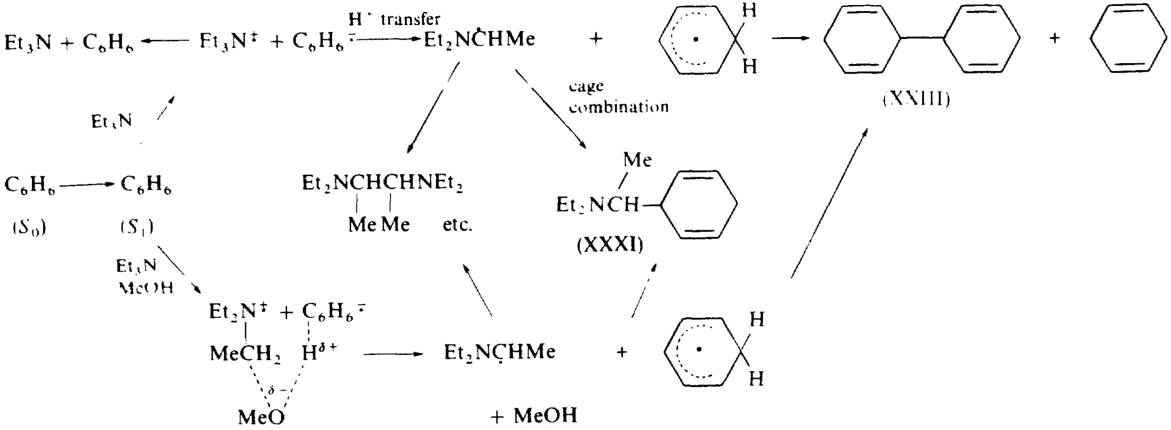
(XXXIII)



(XXXIV)

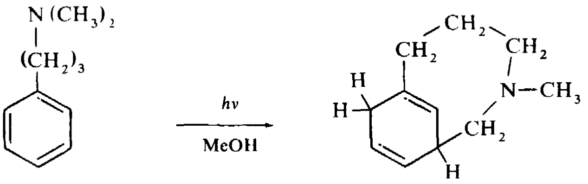
The mechanism proposed for the photoaddition of triethylamine to benzene in the presence of methanol is shown in *Scheme 2* below. The mechanisms for primary and secondary amines are doubtless closely similar, the amines themselves acting as proton-donors.

I conclude by referring to some intramolecular analogues of these tertiary amine additions which have recently been investigated by Dr Klunklin[24].

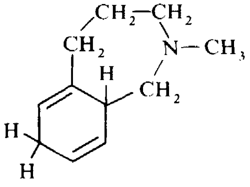

Et₃N + C₆H₆
Et₃N⁺ + C₆H₆⁻
H⁺ transfer
Et₂NĊHMe
+
H
H
+
(XXIII)
Et₃N
C₆H₆
C₆H₆
(S₀)
(S₁)
Et₂NCHCHNEt₂
Me Me
etc.
cage combination
Me
Et₂NCH
(XXXI)
Et₃N
MeOH
Et₂N⁺ + C₆H₆⁻
MeCH₂
H^δ+
δ−
MeO
Et₂NĊHMe
+
H
H
+ MeOH

Scheme 2

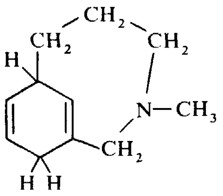
He has observed that the amines $Ph(CH_2)_nNMe_2$ show marked fluorescence emission (λ_{max} 280–330 nm), in the cases where $n = 2, 3, 4$, and most intensely where $n = 3$. This emission does not appear in the case where $n = 1$, and seems most reasonably attributable to an intramolecular exciplex formed by charge-transfer between the amine and benzene moieties. Irradiation in the presence of methanol gives intramolecular adducts, e.g. (XXXV), by attack on the *meta* positions. The isomeric adducts (XXXVI) and (XXXVII) were not found.



(XXXV)



(XXXVI)



(XXXVII)

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It is a pleasure to record my indebtedness to many past and present students and collaborators whose names are given in the text and references, and in particular to my colleague Dr A. Gilbert.

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