Tetrahedron Vol 33, pp 2459 to 2490 Pergamon Press 1977 Printed in Great Britain

# TETRAHEDRON REPORT NUMBER 40

# THE ORGANIC PHOTOCHEMISTRY OF BENZENE—II

D. BRYCE-SMITH* and A. GILBERT
Chemistry Department, University of Reading, Reading, Berkshire, England

(*Received for publication* 30 *July* 1976)

## 1. INTRODUCTION

In Part I[1] of this two-part review of the organic photochemistry of the benzene ring, we were largely concerned with general principles, especially orbital symmetry aspects, and their application to photoisomerisation processes. Our intention in this second part is to cover principally the photoreactions of the benzene ring with other molecules. These reactions are mostly additions, particularly, but not exclusively, cycloadditions. It will be seen that certain examples of photoelectrophilic substitution into the benzene ring have an interesting mechanistic relationship to some of the photoadditions of electron acceptor addends. On the other hand, photonucleophilic substitution is not broadly covered, partly because it is the subject of excellent recent reviews by Havinga and Cornelisse,[2] pioneers in this field, and partly because it is a process in which attention is more directed towards the substituents on the benzene ring than the ring itself. However, one or two examples of photonucleophilic substitution into benzene will be found in the section dealing with photoaddition of amines. We have not included processes of predominantly radical type (e.g. the photo-Fries reaction, photolysis of iodobenzenes) where absorption of a quantum leads to homolysis of a bond in or involving a ring substituent, rather than the ring itself. As in Part I we are largely concerned with monocyclic compounds, and processes which involve naphthalene, etc. are only mentioned when they are of particular relevance to the benzenes. Extensive discussions of the literature relating to radical aspects, the stilbene-phenanthrene and related conversions, and the photochemical reactions of polycyclic and heterocyclic aromatic compounds will be found in the annual Volumes of Ref. 3.

In general, we may classify the photoaddition reactions of the benzene ring into three broad mechanistic types:

(a) reactions of the photo-excited benzene (usually $S_1$) with another molecule in its electronic ground state;

(b) reactions of ground-state benzene with another electronically excited molecule;

(c) reactions between donor–acceptor pairs which involve either excitation through absorption in a charge-transfer band of a molecular complex or formation of a complex (exciplex) between one excited molecule (normally $S_1$) and another ground state molecule.

Reactions of type (a) and (b) are not usually sensitive to the polarity or acidity of the medium, but those of type (c) involve charge-transfer leading to the transient formation of markedly polar intermediates, and often show an interesting dependence on the presence of proton-donors and/or solvent polarity. In some cases reactions can be directed into a completely different pathway by the introduction of a proton-donor: the photoaddition of maleic anhydride to benzene is an example of such an acid-sensitive process (Section 3.1.3).

The absorption characteristics of benzene given in Part I[1] are relevant to the following discussions. As far as is known, all the photoreactions of benzene with other species involving excitation of the ring result from absorption within the first optical transition, and this is accomplished very conveniently by use of 254-nm radiation (low pressure mercury lamp).

## 2. DIMERISATION PROCESSES

The first report of the photodimerisation of an aromatic molecule appeared in 1866 and was concerned with the anthracene photo-dimer(I).[4] Numerous subsequent accounts have described the photochemical behaviour of anthracene and its derivatives both in solution and the crystalline state; the dimers have all structures of type **1** and excimers have been implicated as their precursors.[5] More recently the photodimerisation of phenanthrenes (to give products of type **2**)[6] and of $\beta$-alkoxy-[7] and $\beta$-cyano-[8] naphthalenes (to give products of types **3** and **4**) have been reported, and the corresponding intramolecular reactions have been observed with several systems.[9] Biphenylene is reported to yield the cyclobutane dimer **5** on irradiation of the monomer in refluxing hexane.[10]

Despite the generality of the reaction with polycyclic aromatic compounds we know of no corresponding examples involving uncondensed benzenoid aromatic rings (see, however, Refs. 11 and 12 for the photodimerisation of 2-aminopyridine and 3-oxido-1-phenylpyridinium). But the formation of a benzene excimer (excited dimer) plays an important part in certain photophysical processes, for example as a precursor of $T_1$ benzene.[13] In this context it is interesting that the 1,2-, 1′,2′-dimer **6** of benzene has been synthesised indirectly from a $C_{12}H_{12}$ isomer: it has limited thermal stability and readily dissociates to benzene.[14] An analysis of the orbital symmetry factors in the photodimerisation of benzene suggests that the concerted dimerisation to give **6**, **7** or **8** is only allowed from $B_{1u}$ ($S_2$ or $T_1$) benzene.[15] It is worth noting that in principle dimerisation could also arise via a 1,3-cycloaddition process (cf. alkene addition, Ref. 16). Thermal dissociation of the 1,2-/1′,4′-dimer (**8**) is allowed as a concerted process, so this as yet unknown molecule is expected to be less thermally stable than **6** and the unknown 1,4-/1',4'-isomer (**7**).[15] It is interesting that although hexafluorobenzene and benzene form a well-defined 1:1 "dark" complex,[17] irradiation gives no dimers but leads instead to 2,3,4,5,6-pentafluorobiphenyl:[18] the reaction has some interesting mechanistic features, and is discussed in Section 4.

It is relevant to this discussion that the triplet yield of benzene increases with concentration. This effect is commonly attributed to a greater efficiency of intersystem crossing in the excimer than in $S_1$ benzene: the triplet excimer then decays to $T_1$ and $S_0$ benzene.[13] In veiw of the precursor role of excimers in the dimerisation of polycyclic aromatic compounds, and the observations that dioxetanes yield triplet excited ketones,[19] it is interesting to speculate that the benzene excimer may indeed transform into a transitory chemical dimer such as **7** or **8** which then dissociates into $T_1$ and $S_0$ benzene: simple thermochemical calculations suggest, however, that decomposition of the dimers (**6**, **7** or **8**) to $T_1$ benzene would be endothermic by *ca.* 67 kJ mole$^{-1}$, and therefore unlikely to occur.[20]

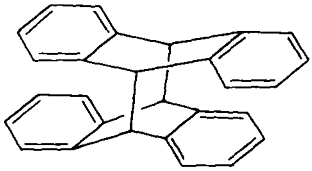
### 3. PHOTOADDITION REACTIONS OF BENZENE

If one excludes catalytic hydrogenation and the initial addition stage of substitution processes, thermal addition reactions of the benzene ring are few and far between. In contrast many accounts have appeared since 1959 which describe novel light-induced additions of a variety of molecules to benzene. Such addends include ethylenes, acetylenes, dienes, aliphatic amines, diethyl ether, trifluoroacetophenone, alcohols and carboxylic acids; some of the reactions are of synthetic utility. As we indicated in Part I, however, some seemingly light-induced addition reactions of benzene actually involve thermal addition of the addend to photo-produced benzvalene: such reactions include the 1,3-addition of alcohols and water,[21] and indeed the "photo-oxidation" of benzene. There has been some controversy over this latter process, and particularly over the structure of the product. Structures **9**[22] and **10**[23] have both been considered, and apparently supported, but the bulk of the information favors **9**.[24] In this context, it is pertinent to note that whereas benzene does not yield a transannular photoperoxide on irradiation in the presence of molecular oxygen, many anthracene and naphthalene derivatives do so. The point of attack is dependent upon the substituent, and mechanistic studies[25] show that the triplet arene transfers energy to molecular oxygen which, now in its singlet state, undergoes thermal addition to the $S_0$ hydrocarbon to give, e.g. **11** from anthracene. Thus the process is related to the dye-sensitised photo-oxidation of 1,3-dienes. An excellent review of the pre-1969 literature on photo-oxidation of polycyclic aromatic compounds has been published,[26] and more recent reports are summarised in the annual Volumes of Ref. 3. Certain styrenes, including indene, undergo photo-oxidation by a mechanism involving singlet oxygen which appears to involve the initial formation of an unstable cyclic peroxide of type **12**,[27] and the reaction of singlet oxygen with 9,10-dimethoxyphenanthrene is interpreted in terms of the transitory formation of the dioxetan **13**.[28]

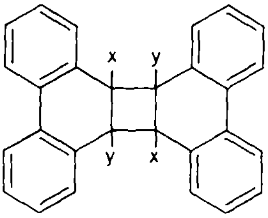
#### 3.1 *Addition of ethylenic compounds to benzene*

Irradiation of benzene at 254 nm in the presence of ethylenes can lead to the formation of 1,2-, 1,3- and 1,4-cycloadducts **14**, **15** and **16** respectively: in the case of 1,1-dimethylethylenes, products **17** of an "ene-type" 1,4-reaction with the benzene also result. Only with a very few systems have all types of cycloadduct been observed, and with many ethylenes one mode of reaction greatly predominates. The highly varied reactions of benzenes with a wide variety of ethylenes present an apparently chaotic picture, but order is now beginning to emerge following recognition of the importance of (*a*) orbital symmetry factors[15] and (*b*) the difference in ionization potentials between the reacting species.[16] For all modes of cycloaddition the stereochemistry of the ethylenic addend is preserved in the products.[29–32] It is generally accepted that for addition of simple alkenes, the lowest excited singlet state ($S_1$) of benzene is the excited species leading to reaction,[29,30] although it has been postulated that the species immediately prior to the addition process may be an alkene-benzene exciplex:[30,33] cf. the role of excimers in photodimerisation reactions, to which allusion has already been made. Figures 1–4 illustrate the orbital symmetry correlation diagrams for 1,2-, 1,3- and 1,4-cycloadditions and are constructed as outlined in Part I.[1] From such considerations it transpires that only the concerted 1,3-addition is symmetry allowed from $S_1$ benzene and $S_0$ alkene, and that concerted 1,2- and 1,4-cycloadditions are symmetry forbidden from such interactions unless mixing with charge-transfer states occurs.[15] Concerted homopolar 1,2- and 1,4-cycloadditions require either electronically excited ethylenes ($S_1$ or $T_1$) to react with $S_0$ benzene, or $S_0$ ethylene plus benzene of $B_{1u}$ symmetry (i.e. $S_2$ or $T_1$ benzene). But as discussed in Refs. 29 and 30, the addition reactions are found to occur via $S_1$ benzene; and indeed for simple alkenes, the $S_1$ states of the addend are comparatively inaccessible at 254 nm in the presence of the more strongly absorbing benzene. Only acetylene appears to add to benzene in this way,[34] i.e. via $S_1$ acetylene, but the chemical and quantum yields are very low in comparison with those for the corresponding additions of alkenes where, although variable, the quantum yields can approach unity.[16] On the other hand, this mechanism can apply for ethylenic addends bearing substituents which reduce the level of the $S_1$ state below that of $S_1$ benzene, as with maleimide, for example. Mixing of states as would occur in either a ground or excited state complex (i.e. an exciplex) however, relaxes the orbital symmetry dictates. Thus the observation of stereospecific 1,2-, 1,3- and 1,4-cycloaddition of, for example, the *cis*- and *trans*-but-2-enes to $S_1$ benzene, has been rationalised in terms of an exciplex between the alkene and the excited benzene.[30,35] It is worth noting here that in addition reactions involving donor–acceptor pairs, it appears possible to have a substantially stereospecific non-concerted addition in which the stereospecificity arises by coulombic interactions in a dipolar intermediate.[36]

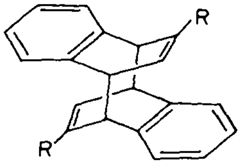
3.1.1 1,3-*Cycloaddition of ethylene to benzene.* The intriguing 1,3-cycloaddition of simple alkenes and cycloalkenes to benzene to give adducts of type **15** was discovered independently by two groups.[37,38] Although the 1,3-addition is stereospecific with respect to the alkene, both *exo* and *endo* isomers of **15** are formed in many cases.[31,39] Isomers with an *endo*-hydrogen at C-7 are labile at temperatures around 300°C and yield bicyclo(3,3,0)octa-2,7-diene derivatives (**18**) by way of a Woodward–Hoffmann thermally allowed suprafacial 1,5-sigmatropic rearrangement.[31,41,42] At higher temperatures, the corresponding *exo*-isomer undergoes a vinylcyclopropane rearrangement which effectively turns



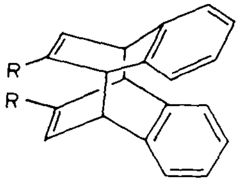
(1)



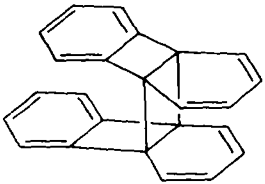
(2)



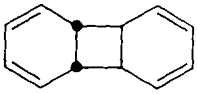
(3)
R = OMe or CN



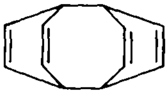
(4)
R = OMe or CN



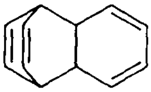
(5)



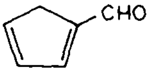
(6)



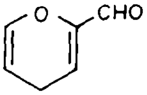
(7)



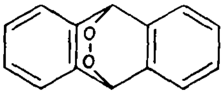
(8)



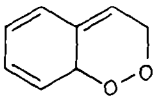
(9)



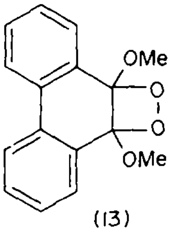
(10)



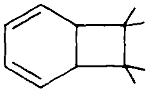
(11)



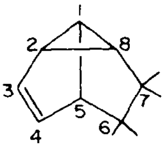
(12)



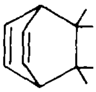
(13)



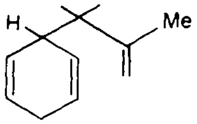
(14)



(15)



(16)



(17)

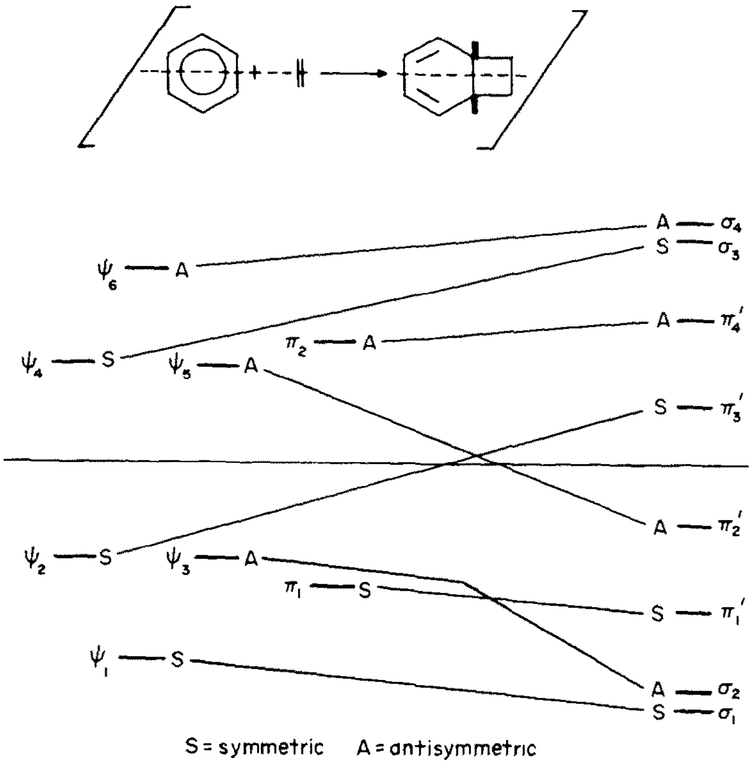
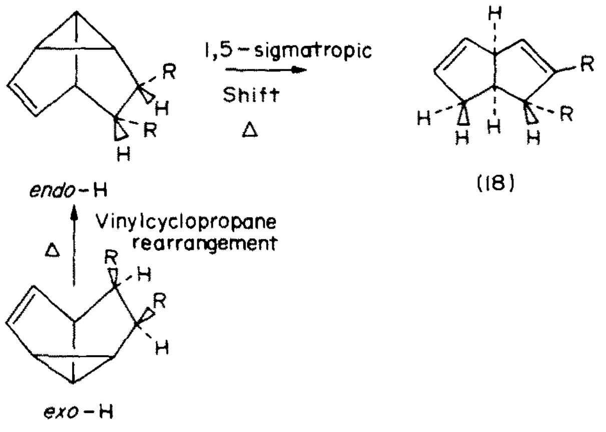


Fig. 1. 1,2-Cycloaddition of ethylene to benzene. *Note.* Orbital symmetries in benzene are as in Part I.

the molecule "inside out". Thus the molecule with an *exo* hydrogen at C-6 forms the isomer having hydrogen *endo* at C-7, and thence the bicyclic diene (Scheme 1).[41] This differential thermal lability is a useful method for estimating the relative amounts of *exo* and *endo* adducts, particularly those from *cis*-1,2-disubstituted ethylenes, and has been used to good effect in assigning the structures of the 1,3-cycloadducts of *cis*- and *trans*-but-2-ene with benzene.[41] Thus the major product from *cis*-but-2-ene is unchanged after heating for 20 hr at 300°C whereas the minor adduct is converted into **19**. Similarly the minor isomer **20a** from the *trans*-alkene gives **21**: the major product (**20b**) is relatively thermally stable, although at higher temperatures it undergoes a vinylcyclopropane rearrangement to yield **21** via **20a**.

Figures 2 and 3 show the correlation diagrams for the 1,3-cycloaddition process and illustrate that the "allowedness" of this reaction is insensitive to such mechanistic details as the relative timing of the three bond-formation steps. Thus bond (*a*) may be formed prior to bonds (*b*) and (*c*) (Fig. 3), or subsequently (Fig. 2), or all three may be formed synchronously.[32] The stereospecificity of the reaction and the insensitivity to proton donors and solvent polarity indicate that bonds (*b*) and (*c*) at least are formed in an essentially concerted step.

Simple ethylenic compounds which have been observed to undergo 1,3-cycloaddition to benzene as apparently the most efficient mode of reaction are *cis*- and *trans*-but-2-ene,[30] cyclobutene,[43,44] 2,3-dimethylcyclobutene,[45] methylenecyclobutane,[46] 2,3-dichlorocy-



Scheme 1.

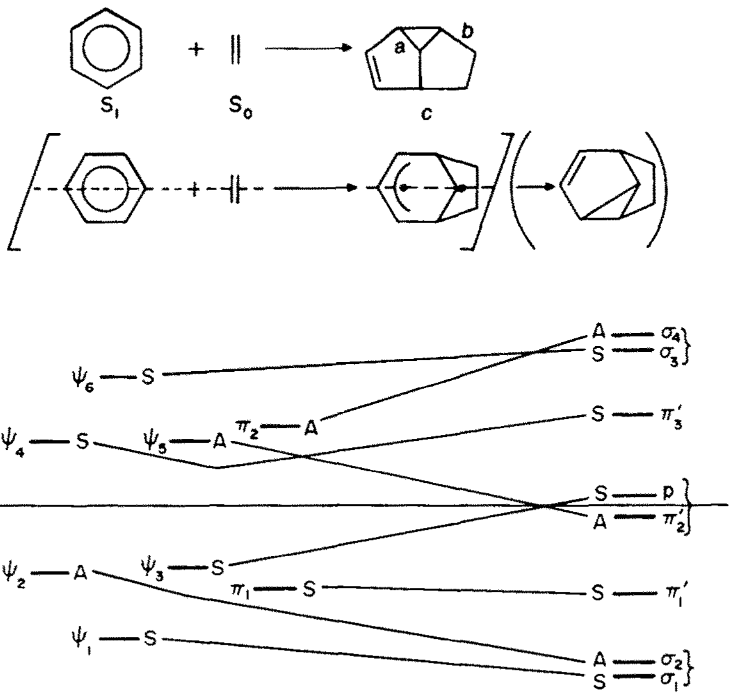


Fig. 2. 1,3-Cycloaddition of ethylene to benzene.

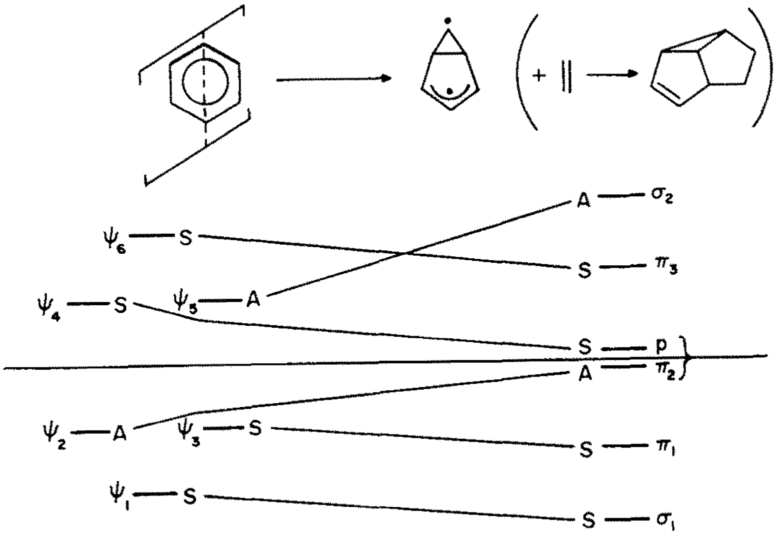


Fig. 3. 1,3-Bonding in benzene.

clobutene,[47] bicyclo-[3,2,0]-hepta-2,6-diene,[45] norbornene[40] (but not norbornadiene),[48] 5,6-dichloronorbornene,[49] cyclopentene,[37,44,50] cyclohexene,[16] cycloheptene,[16] *cis*-cyclo-octene,[16,38] *cis*-cyclononene,[16] cyclohexa-1,4-diene,[51] penta-1,4-diene,[51] isobutene,[51] 2-methylbut-2-ene,[51] vinyl acetate,[52] vinylene carbonate[53] and pent-1-en-4-ol.[52] Indeed the 1,3-cycloadduct itself may act as the alkene component in this system, thereby giving telomers of benzene residues.[54]

As stated earlier, the stereochemistry of the ethylene is preserved in the product. However, the relative amounts of the *exo* and *endo* isomers depend upon the ethylene, although the *endo* isomer predominates in many cases. The reaction also shows no apparent regioselectivity with simple alkenes; thus isobutene gives both the 1,3-cycloadduct isomers in approximately equal amounts.[51] Photochemical 1,3-cycloaddition has been extended to a number of systems involving simple alkenes and substituted benzenoid compounds.[52,55–59] In the case of methylbenzenes, the attack of either cyclobutene or cyclopentene is remarkably specific and preferentially yields the 1,3-cycloadducts with the 1-position substituted.[55,56] The model of the exciplex which is suggested to account for these observations contains an *endo* sandwich structure **22** in which the ethylenic $\pi$-electrons are exactly above a 1,3-pair of car-

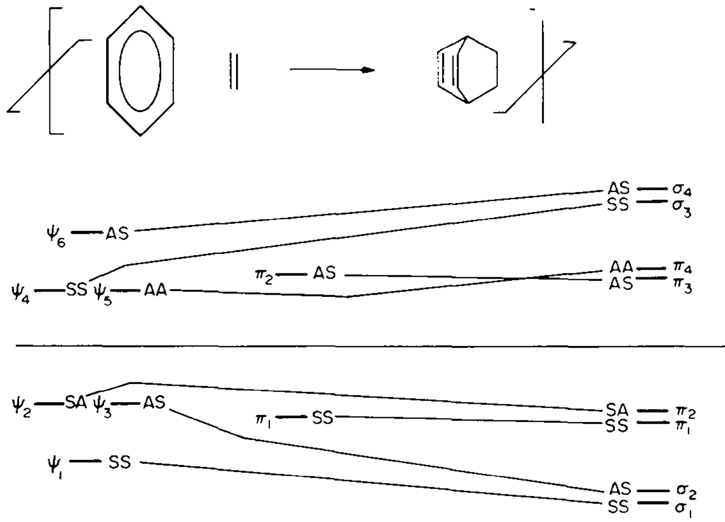
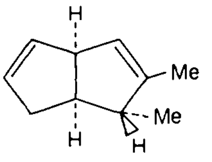


Fig. 4. 1,4-Cycloaddition of ethylene to benzene.

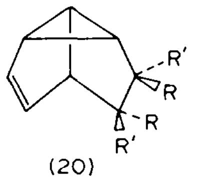
bons in the aromatic ring. Consistent with this is the observation that not only are the *exo* adducts generally less favoured with benzene, but that with methylbenzenes and cyclobutene and cyclopentene only the *endo* adducts are detected. This knowledge of the specificity of attack has been used in a synthesis of (4,4,3) propellanes (**23**) from the adduct **24** of cyclopentene and tetralin.[59] With *cis*-cyclo-octene as the ethylene, however, the process is not quite so specific and both *exo* and *endo* isomers (ratio 1:7) **25** and **26** are formed from toluene; but in this case the methyl group is located on the 5-position.[58] The two major adducts from *o*-xylene and *cis*-cyclo-octene have *endo* stereochemistry with the methyl groups in the 1,5- and 1,8-positions, whereas the orientations of the groups in the corresponding 1,3-*endo* adducts from *m*-xylene are 2,4- and 3,8- (30 and 35% of the adduct mixture respectively). The major product from *p*-xylene and *cis*-cyclo-octene has *endo* stereochemistry with the methyl groups in the 1,3-positions (numbered as in **15**).[58] We have noted earlier that there are at least two variants of the mechanism by which the 1,3-cycloadducts may arise, but whether the above stereochemical differences reflect a change in the details of the adduct forming process remains to be seen. If the "prefulvene" diradical (**27**) is an intermediate in the formation of the 1,3-cycloadducts, it would be expected that products substituted in the 5- and 8- positions of **15** would predominate as corresponding substitution in **27** would stabilise the radical centres. The failure to obtain the 5,8-dimethyl derivative of **15** from *m*-xylene and cyclic ethylenes would therefore argue against the intermediacy of **27**; but on the other hand it is noteworthy that the adducts from *cis*-cyclo-octene and both toluene and *o*-xylene do have substitution at either the 5- or 8-positions.[58]

An intramolecular analogue of the foregoing 1,3-cycloaddition processes is known. Thus irradiation of 6-phenylhex-2-ene yields **28** and **29** from the *cis*-ethylene and **30** from the *trans* isomer.[33] The authors suggest the intermediacy of an intramolecular exciplex between the $S_1$ phenyl group and the $S_0$ alkene moiety. The rapid formation of this is considered to be responsible for the diminished singlet lifetime and fluorescence of the phenyl moiety.

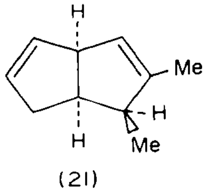
Although the 1,3-addition of ethylenes to the benzene ring provides a convenient and versatile route to a wide



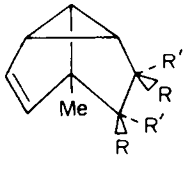
(19)



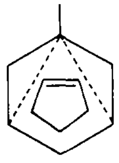
(20)
*a* R=H, R'=Me
*b* R=Me, R'=H



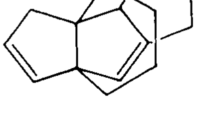
(21)



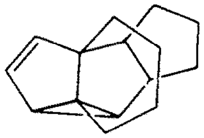
(25) R=H, R'-R' = $-(CH_2)_6-$
(26) R-R = $-(CH_2)_6-$, R'=H



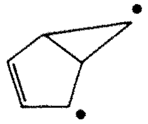
(22)



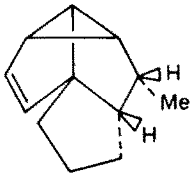
(23)



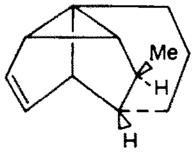
(24)



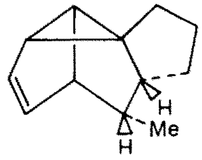
(27)



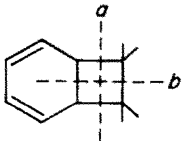
(29)



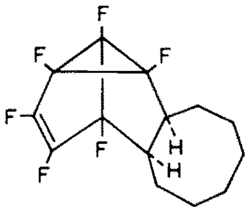
(30)



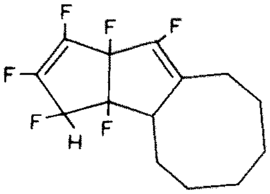
(28)



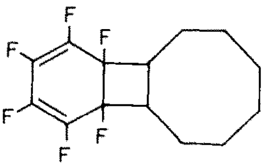
(31)



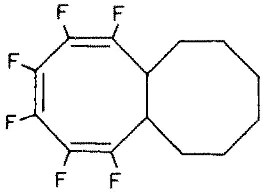
(32)



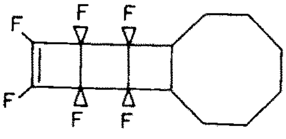
(33)



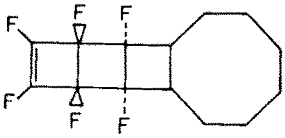
(34)



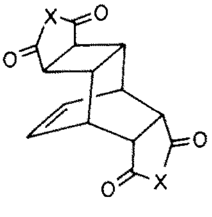
(35)



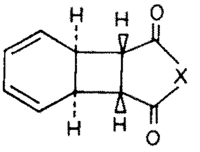
(36)



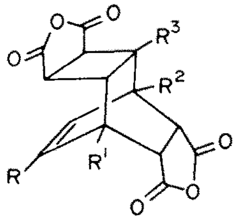
(37)



(38) *a*, X=O
*b*, X=NH
or N–R



(39) *a*, X=O
*b*, X=NH or NR



(40) R=Ph, $R^1=R^2=R^3=H$
(41) $R=R^3=H$, $R^1=R^2=Me$
(42) $R=R^3=Me$, $R^1=R^2=H$

variety of dihydrosemibullvalenes, acetylenes, which might have been expected *a priori* to give the corresponding semibullvalenes, do not in fact react in this manner: in general, they undergo 1,2-cycloaddition to benzene, and thereby give cyclo-octatetraenes as the end products following valence isomerisation of the initial cycloadducts (Section 3.2).

3.1.2 *1,2-cycloaddition of ethylenes to benzene.* Many ethylenic compounds give minor proportions of 1,2-cycloadducts with benzene, in comparison with the 1,3-cycloadducts, but in some cases the 1,2-cycloadducts predominate.[16,30,60,63]

As with 1,3-cycloaddition, the initially excited species in 1,2-cycloadditions is considered to be $S_1$ benzene, and both processes are highly stereospecific with respect to the ethylene in all cases so far studied. How then does one reconcile these findings with the orbital symmetry prediction[15] that only the 1,3-process is allowed as a concerted reaction? A key point to be kept in mind is that the orbital symmetry analysis applies only to processes in which no significant mixing with charge-transfer states occurs. Thus although it may well be applicable to those systems having no marked donor–acceptor character, its rigour is expected to diminish as the polar character of the systems increases; but the stereospecificity may still be preserved by coulombic interactions, as we have previously noted. These considerations led us to conclude that the "forbidden" 1,2-cycloadditions of ethylenes should occur most readily in those systems having markedly donor–acceptor character, and that in other systems the "allowed" 1,3-addition process should predominate. It may be said right away that these expectations have been confirmed to a most gratifying extent by systematic experimental studies.[16]

In particular, the effect of polar factors to render the 1,2-cycloadditions "allowed" has been investigated by varying the donor and acceptor properties of the ethylenes relative to those of the benzenes. Ionisation potentials have been used as a convenient measure of these properties, the important factor being the *difference* in I.P. between the reactants. One may note that polar factors should also promote addition through the more favourable entropy of activation which could result from sterically favourable molecular associations of a coulombic nature between the reactants in the excited or ground states.

With the $C_5$–$C_9$ cycloalkenes, 1,3-cycloaddition always occurred, but 1,2-cycloadducts were only observed with the *cis*- and *trans*-cyclo-octenes (see Table 1). These two cycloalkenes have the lowest ionisation potentials in this series, i.e. they are the strongest donors.[16] Further, the quantum yield for 1,2-cycloaddition with *trans*-cyclo-octene (I.P. 8.51 eV) and benzene (I.P. 9.24 eV) was 0.37, whereas the corresponding value for the *cis*-cycloalkene (I.P. 8.75 eV) was 0.09, and only 1,3-addition with no detectable 1,2-addition was observed between these cycloalkenes and the weaker acceptor toluene (I.P. 8.82 eV). These findings accord with the much earlier observation that simple ethylenes yield only 1,2-cycloadducts with the strong acceptor arene, benzonitrile[61] (I.P. 9.71 eV) (although reaction of the nitrile function has also subsequently been observed with donor olefins[62]).

Table 1.

| Ethylene | Ionisation potential (ev) | $\Phi_{1,2}$ | $\Phi_{1,3(\text{total})}$ |
|---|---|---|---|
| Cyclopentene | 9.02 | — | 0.19 |
| Cycloheptene | 8.86 | — | 0.27 |
| *cis*-Cyclononene | 8.87 | — | 0.13 |
| *cis*-Cyclo-octene | 8.75 | 0.09 | 0.38 |
| *trans*-Cyclo-octene | 8.51 | 0.37 | 0.28 |
| 2,3-Dimethylbut-2-ene | 8.30 | 0.25 | 0.03 |
| (Benzene) | 9.24 | | |

They strongly imply that the 1,2-addition of ethylenes to $S_1$ aromatic compounds necessarily involves an element of charge transfer between the addends. The stereospecificity could result from charge-correlation rather than true concertedness, as has been suggested for certain cycloadditions of ethylenes to quinones.[36] Support for this proposal is found from studies with other systems. For example, 1,2-cycloaddition to benzene is the major process with the *donor* ethylenes dihydropyran,[63] *trans*-1,2-dimethoxyethylene,[16] 1,1-dimethoxyethylene,[49] tetramethylethylene,[16] and ethyl vinyl ether,[16] and is the sole process detected on irradiation of benzene with the *acceptor* ethylenes methyl vinyl ketone,[16] maleimide,[16] maleic anhydride[16] and acrylonitrile.[64] It also appears significant that the 1,2-addition reaction of at least some of the donor ethylenes is markedly promoted in polar solvents whereas the 1,3-process has been found to be unaffected by change in solvent or addition of proton donors in all cases so far examined.[16,63]

The stereochemical aspects of 1,2-addition are particularly interesting. Firstly, whereas 1,3-cycloaddition leads to both *exo* and *endo* adducts in almost all cases, ethylenes of marked donor or acceptor type relative to the aromatic compound give only a single *endo* or *exo* 1,2-adduct with benzene, at least in all those cases which have been studied.† Secondly it has been found that the donor ethylenes yield *endo* 1,2-adducts, whereas those with acceptor properties add *exo*.[16,30,66–68] Where *endo* addition would be expected from this relationship but is sterically hindered by substituents, as with the donor ethylenes *cis*-di-t-butylethylene (I.P. 8.71 eV) and *cis*-1,2-dimethoxyethylene (I.P. 7.97 eV), it is remarkable that neither the hindered *endo*-addition nor the unhindered *exo*-addition occurs.[16]

It is most satisfying that NMR spectroscopic data provide evidence for stereospecific *ground state* interactions between ethylenes and benzene which exactly match the *exo* or *endo* specificities found in the corresponding 1,2-photoaddition reactions.[69] Unless this match is a coincidence—which seems highly improbable—it appears reasonable to conclude that the stereochemistry of the 1,2-cycloadditions may actually be determined by the stereochemistry of weak precursor complexes.

The foregoing experimental findings and symmetry considerations have been summarised in the following rule,[16] viz. that the quantum yield for 1,2-cycloaddition of an ethylene to benzene is greater than that of the 1,3-process when the ionization potential of the ethylene is either greater than 9.6 or less than 8.65 eV. Thus for ethylenes which have ionisation potentials approximately similar to that of benzene, 1,3-cycloaddition is predicted to have a quantum yield larger than that for the corresponding 1,2-cycloaddition reaction (see, e.g. Ref. 52). Although 1,4-photochemical cycloaddition to the ben-

---

†Dichlorovinylene carbonate gives 1,2-cycloadducts with benzene;[65] but in this case, the stereochemical distinction between *exo* and *endo* addition is obscure (see Section 3.1.7).

zene ring is rather more uncommon than the 1,2-process (see next Section) the two reactions are expected to be closely similar in mechanism.[15]

The above rule has proved to be very useful for predicting the behaviour of untried systems, but one supposed exception to it has appeared. Thus in a recent report on the photoaddition of vinylene carbonate (I.P. 10.08 eV) to benzene it is claimed that the major products are adducts of the 1,3-type under the conditions employed, and that this finding is in conflict with our proposed rule specified above.[53] It is however, most important to realise that this rule referred to quantum and not chemical yields: as no quantum yields were given for the vinylene carbonate additions, the results are not strictly pertinent to the validity or otherwise of this rule. Further it is essential that quantum yield measurements should be made at very low reactant conversions. The reason for this is that in cases where 1,2- and 1,3-cycloadducts are formed between an ethylene and benzene, the former adduct often reaches a photostationary concentration very rapidly whereas the amounts of 1,3-adducts increase progressively with time. This behaviour can be readily understood since most 1,2-cycloadducts are photolabile, and can undergo both direct and triplet benzene-sensitised decomposition to starting materials (*a*-type cleavage in **31**) together with ring opening reactions to yield polyene compounds (*b*-type cleavage in **31**), whereas the 1,3-cycloadducts are relatively photostable. The stationary state of the 1,2-adduct is so low in some systems that its detection at quite low reactant conversions is difficult and only the 1,3-cycloadduct is clearly evident. The extent of triplet benzene-sensitised dissociation of the 1,2-adducts can be minimised by working at high concentrations of the ethylenic addend and/or by incorporating a diluent. Such procedures reduce the benzene concentration and thereby reduce the production of triplet benzene from dissociation of the benzene excimer.[15] The experiments on the vinylene carbonate-benzene system reported in Ref. 53 were carried out using 1.0 M vinylene carbonate in benzene, and to approximately 10% conversion. Under such conditions it is our opinion that it is very likely that the relative concentration of any 1,2-cycloadduct could have been so low as to escape identification. But we recognise from personal experience that the vinylene carbonate-benzene system is in practice a difficult one with which to work.

Although the photoaddition reactions of naphthalene and other polynuclear aromatic hydrocarbons are strictly beyond the scope of the present review, it should be realised that the proposals relating to benzene may not be applicable to other aromatic systems. Thus the two cycloadducts of acrylonitrile and naphthalene result from 1,2-cycloaddition, both have *endo* stereochemistry.[70] It would be of interest to determine whether the corresponding ground state molecular complex is also of *endo* type.

As outlined above, a number of simple benzenoid derivatives undergo both 1,2- and 1,3-cycloaddition of ethylenic compounds. Hexafluorobenzene (I.P. *ca.* 10.4 eV) is a stronger acceptor than benzene. It is therefore somewhat surprising that irradiation of a mixture of *cis*-cyclo-octene and hexafluorobenzene yields a number of adducts[71] of which **32**, **33**, **34** and **35** are apparently the primary products. These are formed from equimolar solutions with quantum yields at 254 nm of 0.14, 0.18, 0.11 and 0.08 respectively: all quantum yields were increased by approximately 50% when 231 nm radiation was used. The direct light-induced formation of **33** from hexafluorobenzene and *cis*-cyclo-octene is noteworthy as this product might have been expected to be thermally derived from **32** by a 1,5-sigmatropic shift: its formation as a "primary" product might arise via **32** formed in a vibrationally excited state in the photoaddition reaction.[31,71] Thus the quantum yield ratio for 1,2- reaction to 1,3-cycloaddition in this reaction is 0.19: 0.32 at 254 nm, and 0.27: 0.47 at 231 nm.[72] (From the corresponding studies with benzene, a higher proportion of 1,2-cycloaddition would have been expected from an addend where the ionisation potential difference is *ca.* 1.6 eV; but no studies have yet been made on possible ground-state complexation between hexafluorobenzene and alkenes, or on the formation of exciplexes.) Further irradiation of this system following formation of the primary products results in the conversion of **34** and **35** into a mixture of **36** and **37**: this transformation occurs more rapidly in $C_6F_6$ solution than by direct irradiation of **34** and **35**, and is thermally reversible.[72]

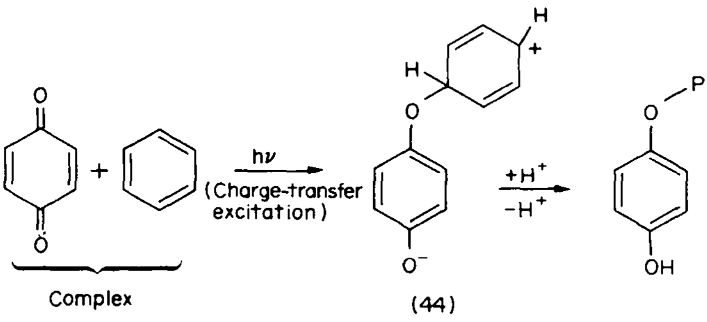
3.1.3 *Photoaddition of maleic anhydride and related dienophiles to benzenoid compounds.* The photoaddition to benzene of the thermal dienophiles maleic anhydride, maleimide, and N-substituted maleimides has already been briefly mentioned. We now consider these cases more fully. The reaction of maleic anhydride was in fact the first photoaddition to benzene to be discovered, and there has been much work and discussion over the past 16 years or so concerning the mechanistic details of the process.[32,73,74] Maleic anhydride and certain maleimides yield 2:1 adducts **38** from irradiation of their benzene solutions both in the absence and presence of triplet sensitisers:[73–76] the sensitiser triplet energy for the maleic anhydride-benzene addition must be greater than 66 kcal/mol.[74e] The 2:1 adduct (**38a**) has remarkable thermal stability and does not melt until 357°C. The mechanisms for the formation of **38** will be discussed in detail below, but we feel it advantageous here to point out that **38** arises via initial 1,2-photoaddition of the dienophile to benzene to give the *exo*-cyclobutane adduct (**39**): this is followed by thermal Diels–Alder *endo* cycloaddition of a second molecule of the dienophile to form the 2:1 adduct.

The structural similarity of the photoadducts from maleic anhydride and maleimide tends to conceal some important mechanistic differences between the reactions. Thus it has been clearly demonstrated in the case of the unsensitised maleic anhydride addition that absorption within the dienophile-benzene charge-transfer band (Fig. 7) is fruitful of reaction,[74d] whereas addition of maleimides to benzene occurs directly without charge-transfer excitation. Indeed maleic anhydride only undergoes cycloaddition to those benzenoid systems with which it forms a ground state complex showing charge-transfer absorption,[77,78] whereas the additions of maleimide are subject to no such restriction.[79] Formation of such a complex, however, does not necessarily mean that photoaddition of maleic anhydride and other strong dienophiles to the benzene ring will occur in practice. For example, neither tetracyanoethylene[78] nor *p*-benzoquinone,[80] both of which form complexes with benzene showing charge-transfer absorption, yields photoadducts, although *p*-benzoquinone gives 4-phenoxyphenol in the presence of acid.[81] Indeed the addition of maleic anhydride to methylbenzenes other than toluene requires triplet sensitisation.[74c,77] The position of attack of maleic anhydride on a substituted benzene is temperature-dependent, and this behaviour may reflect the effect of temperature on equilibria involving the precursor complexes in solution.[82] The adducts from irradiation of maleic anhydride with substituted benzenes at *ca.* 20° have the cyclobutane ring located as far as possible from the benzene substituents. Thus biphenyl gives **40**, yet whereas the two adducts (**41** and **42**) from *p*-xylene are formed in the ratio 20:1 respectively at *ca.* 20°, their ratio is 1:10 at 100° (the stereochemistry of these adducts has not been definitely established but is assumed to be similar to that of the benzene adduct). Such avoidance of substituents in the maleic anhydride and maleimide additions[79,82,83] is noteworthy particularly in view of the fact that corresponding 1,2-cycloadditions of simple olefins to benzonitrile always occur at the 1,2-positions of the aromatic ring.[61] NMR[84] and UV[78] spectroscopic studies have shown that both the "dark" interaction of maleic anhydride with alkylbenzenes and the charge-transfer absorption are influenced by polar and steric factors in ways which closely parallel the photoadditions. In general, the ease of photoaddition of maleic anhydride to substituted benzenes decreases with increasing size and number of the substituents. Electron-withdrawing substituents such as nitro and ethoxycarbonyl in the benzene ring prevent the appearance of charge-transfer absorption with maleic anhydride and totally inhibit the photoaddition process. This dependence of photoaddition on charge-transfer photoexcitation appears to be unique for maleic anhydride.

Following charge-transfer excitation of a ground state complex the next step in the addition of maleic anhydride appears to be the formation of a polarised intermediate which may be depicted as the zwitterion (**43**), this possibly arising from combination of a radical-cation/radical-anion pair. In the presence of a proton donor such as trifluoroacetic acid, the formation of the 2:1 adducts is quenched and a new 1:1 adduct, phenylsuccinic anhydride, is formed although in a poorer chemical yield.[81] This latter reaction may be regarded as an acid-catalysed ***photoelectrophilic substitution process***, zwitterion **43** being analogous to the conventional Wheland intermediate. Thus in a sense, the acid-catalysed photoreaction is analogous to thermal processes of the Friedel–Crafts type; but with the distinction that the photoprocess involves alkylation at the ethylenic moiety of the maleic anhydride, whereas the aluminium chloride-catalysed thermal reaction gives benzoylacrylic acid, i.e. acylation. Although solutions of *p*-benzoquinone in benzene show marked charge-transfer absorption,[80] photoexcitation is not fruitful of reaction. It does however appear that a zwitterionic intermediate such as **44** is formed as irradiation in the presence of a proton donor yields 4-phenoxyphenol, presumably via protonation of the zwitterion (Scheme 2).[81] In the absence of added acid in the proposed zwitterionic intermediate evidently dissociates quantitatively to the starting materials.

When formation of the 2:1 maleic anhydride benzene adduct (**38a**) was first reported, it was suggested that the mechanism involved initial 1,2-cycloaddition of the maleic anhydride to yield **39a**, and that this was followed by a 1,4-thermal Diels–Alder addition.[74a] Attempts to trap such an intermediate as (**39a**) with the powerful dienophile tetracyanoethylene were, however, surprisingly unsuccessful.[73,74e] In view of this, and the necessity for charge-transfer excitation in this system, it was postulated that the intermediate in the process was the zwitterion **43** and that this intermediate reacted directly with maleic anhydride to yield the 2:1 adduct.[81] In such a case the maleic anhydride has to function in the unusual role of a nucleophile, but a literature precedent for this exists in the thermal reaction of maleic anhydride with the benzenonium ion.[85] The postulated bicyclic intermediate (**39a**) has, however, been synthesised,[86] and it has been clearly demonstrated that tetracyanoethylene is surprisingly unreactive towards this diene as a result of steric constraints[86] and doubtless also because in benzene solution tetracyanoethylene is wholly complexed to the aromatic:[78] this complexation lowers its dienophilic reactivity. In the light of these findings and a knowledge of the properties of the 1:1:1 adduct (**38c**) of maleic anhydride, tetracyanoethylene, and benzene, experiments involving more suitable concentrations of reactants have now shown that indeed (as originally postulated[74a,c]) the bicyclic diene (**39a**) is an intermediate in the formation of the 2:1 adduct (**38a**) in both the sensitised and unsensitised processes.[87] Conclusive proof of this has been provided by the total quenching of the formation of **38a** in the presence of N-phenylmaleimide (which was chosen because it only undergoes very inefficient photoaddition to benzene: see Section 3.1.4) and the formation of an equivalent amount of the 1:1:1 adduct **38d**.[88]

It is now evident that the unsensitised addition of maleic anhydride to benzene occurs in the following manner. Excitation of a ground state "charge-transfer" complex gives the zwitterion (**43**) or a polarised species closely akin to this, possibly via a radical-ion pair. In the presence of a proton donor this polarised species is intercepted to give phenylsuccinic anhydride, and the 2:1 adduct (**38a**) does not form. In the absence of a proton donor, **43** cyclises to the cyclobutane intermediate **39a** which can then undergo thermal addition of another



Scheme 2.

molecule of maleic anhydride to give the 2:1 adduct **38a**. In the presence of added dienophiles competitive with maleic anhydride, 1:1:1 adducts and the 2:1 adduct **38a** are formed in proportions dependent upon the dienophilic activity of the added dienophile relative to that of maleic anhydride under the conditions of the irradiation.

The benzophenone-sensitised reaction, and the unsensitised process in the presence of heavy-atom solvents (e.g. $CH_2Br_2$), involve triplet rather than singlet intermediates, and in such cases the presence of proton donors does not have the same dramatic effect as that described above.[88] The observed effects of proton donors and the only slight quenching effect of oxygen[74e] suggest that the unsensitised process (in the absence of heavy atom solvents) occurs largely via a singlet pathway involving the intermediate (**43**) which has greater charge separation than would be expected for the corresponding triplet species, where of course the spin pairing required for zwitterion (**43**) cannot occur. The mechanistic pathway for the photoaddition of maleic anhydride to benzene arising via both $S_1$ and $T_1$ complexes is summarised in Scheme 3. It is pertinent to note here that the 1:1 adduct **39a** has been "trapped" from this system by duroquinone as **45** from benzophenone-sensitised irradiation of the mixed system: the 2:1 adduct **38a** was also formed.[89] The structure **45** was assigned to this 1:1:1 adduct from a comparison of its spectral properties with those of compound **46** which was obtained photochemically from duroquinone and cyclohexa-1,3-diene.[90] In this case, photochemical trapping of the 1:1 intermediate (**39a**) by duroquinone (a very weak thermal dienophile) competes effectively with the normal thermal addition of a second molecule of maleic anhydride. Increasing the concentration of benzophenone or maleic anhydride in the mixed system decreases the ratio of the saturated adduct **45** to **38a**, whereas at lower concentrations of benzophenone, proportionally more of the adduct **45** is formed, but the rate of addition is reduced. Derivatives of benzene bearing electron-withdrawing groups (chloro-, bromo- and fluorobenzenes) have been shown to promote the formation of the saturated 1:1:1 adducts whereas those with electron donating groups (e.g. *o*- and *p*-xylenes) favour the 2:1 adducts. Analogous saturated 1:1:1 adducts of duroquinone and benzene have obtained by the same workers with maleimide and N-ethylmaleimide, and by Deshpande with acrylonitrile, methylmaleic anhydride and dimethylmaleic anhydride.[92] The reaction appears to be quite broad in scope, and provides an extremely simple route to some complex ring systems.

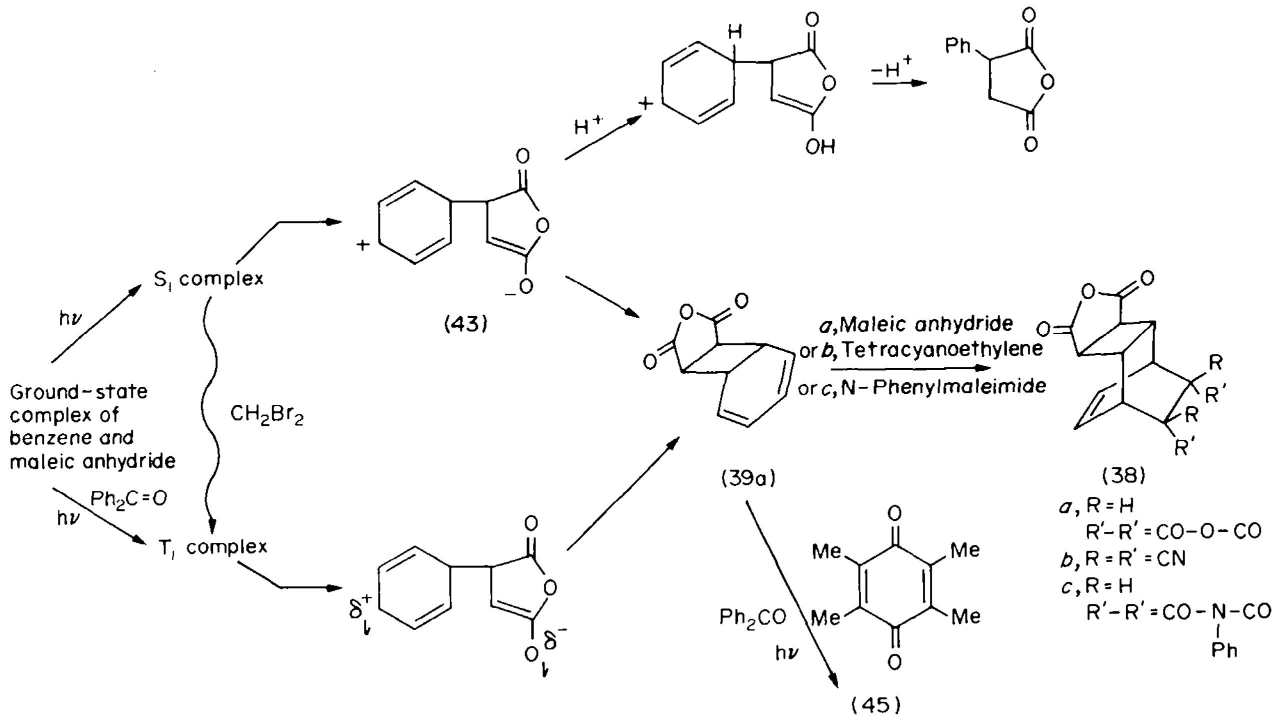
3.1.4 *Addition of maleimides to the benzene ring.* Most of the mechanistic information on the photoaddition of maleimides has been obtained from studies with maleimide itself and the N-n-butyl derivative (which behaves very similarly but is experimentally more convenient). The 1:1 bycyclic adduct **39b** from the maleimide and benzene is readily intercepted by tetracyanoethylene,[73,93] in contrast with the corresponding 1:1 intermediate **39a** from maleic anhydride and benzene. Maleimide is a much weaker dienophile than maleic anhydride, and tetracyanoethylene is better able to compete with it despite the steric and solvation problems to which allusion has previously been made in connection with the addition to **39a**. The addition of maleimide occurs following excitation of the imide† and the reaction is thus wholly consistent with the orbital symmetry analysis in that the 1,2-cycloaddition process is allowed from the $S_1$ or $T_1$ excited states of the maleimide.[15] In this case formation of a ground state complex between the addends may be helpful on entropy grounds, but it is probably not essential.[93] Thus 2:1 photoadducts have been obtained from maleimide and such acceptor compounds as benzonitrile, acetophenone, and methyl benzoate (contrast maleic anhydride which, as previously noted, neither exhibits charge-transfer absorption with, nor photoadds to, benzenes bearing strong electron-acceptor substituents): the major 2:1 adduct from these systems reflects initial 3,4-addition of the maleimide.[79] From quenching studies with oxygen and piperylene, it would appear that attack of the triplet addend yields the intermediate 1:1 bycyclic adduct [cf. addition of dichlorovinylene carbonate to benzene (Section 3.1.7)].[94] The reaction is quenched somewhat by proton donors, probably as a result of imide protonation rather than interception of a polarised intermediate since no phenylsuccinimides have ever been observed to be formed in the presence of proton donors.[81,91] In further contrast with maleic anhydride, maleimide undergoes photoaddition to polyalkylbenzenes in the absence of a triplet sensitiser such as benzophenone,[79] and also undergoes addition to anisole to yield 2:1 adducts which reflect 1,2-, 2,3- and 3,4- initial additions of the imide.[95] No addition was observed between maleic anhydride and anisole—a surprising result, but possibly interaction with the ethereal oxygen leads to complexation stereochemically unfavourable to photoaddition.

The efficiency of the photoaddition of maleimides to benzene is very dependent on the N-substituent.[73,93] The maleimides which efficiently form 2:1 adducts are those which either have no $\pi$-electron system on the N-substituent (H, alkyl), or have a $\pi$-electron system which is prevented from significant overlap with the nitrogen $n$-orbital. This latter effect may be achieved either by the interposition of an insulating $CH_2$ group or by the presence of *ortho* substituents on a phenyl ring which promote a skew configuration of the imide and phenyl rings. Thus whereas N-phenylmaleimide and N-*m*- and *p*-tolylmaleimides give only traces of the corresponding 2:1 adducts with benzene, N-benzyl-, N-*o*-tolyl- and N-2,6-xylylmaleimide react approximately as readily as maleimide itself.[75,93] The failure of the former addends to react efficiently may result from the conjugated $\pi$-electron system acting as an energy sink and its dissipation of energy by a free rotor effect. This idea is supported by differences in the ultraviolet absorption spectra of the maleimides: expressed simply, those maleimides which do not readily photoadd to benzene are yellow whereas those which readily react or are of intermediate reactivity towards benzene are colourless and pale yellow respectively.[73] Irradiation of the yellow maleimides in benzene leads mainly to the corresponding cyclobutane dimers.[73,75,93]

3.1.5 *Miscellaneous 1,2-cycloadditions of ethylenic compounds.* It is interesting that monomethyl- and dimethylmaleic anhydrides resemble maleimide more than maleic anhydride in their photoadditions to benzene. Benzene solutions of these anhydrides show little

---

†Maleimide has a much more strongly absorbing $S_0 \rightarrow S_1$ band ($n \rightarrow \pi^*$) than maleic anhydride, probably as a result of greater mixing with the allowed $\pi \rightarrow \pi^*$ transition, and this extends well beyond the benzene absorption front at *ca.* 270 nm. The maleimide-benzene charge-transfer absorption is hidden under the benzene absorption at *ca.* 230–260 nm and the transition is not significantly excited under the irradiation conditions of this study.[92,93]



Scheme 3. Pathways in the photoaddition of maleic anhydride to benzene.

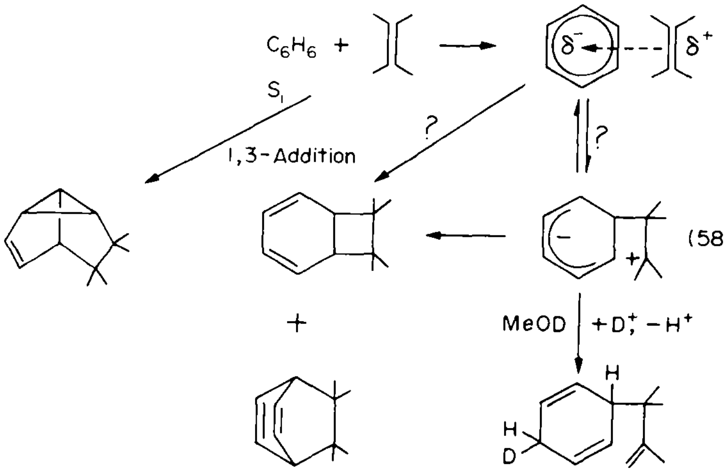
or no charge-transfer absorption, irradiation gives no 2:1 adducts, and proton donors are without effect. These marked differences from the behaviour of maleic anhydride in benzene can be attributed to one or both of two factors: (a) weakening of the acceptor (dienophilic) character of the anhydride by the electron donor effect of the methyl group(s), and (b) weakened or non-existent complexation between the anhydride and benzene as a result of the steric effect of the methyl group(s). Thus the lowest energy excitation in these systems involves essentially "free" methylmaleic anhydrides, as with maleimide, and these may now undergo formation of a 1,2-adduct with benzene by a symmetry-allowed concerted process.[15] But the methylmaleic anhydrides are too weak as dienophiles to intercept the 1:1 intermediates, so no 2:1 adduct is obtained and only a low photostationary concentration of the 1:1 adduct results. On irradiation of methylmaleic anhydride in the presence of either maleic anhydride or tetracyanoethylene the 1:1:1 adducts **47** and **48** respectively are formed, although in the former case approximately similar amounts of the 2:1 adduct **38a** are also obtained.[92] But irradiation of methylmaleic anhydride in benzene followed by addition of maleic and anhydride to the solution in the dark yields **47** as the sole product and hence proves the initial 1,2-photoaddition of methylmaleic anhydride to benzene followed by a thermal 1,4-addition of the maleic anhydride.[92]

Evidence for the addition of dimethylmaleic anhydride to benzene has only been obtained by the trapping of the 1:1 adduct with duroquinone to give a very small amount of **49**.[92] The major product from both this and other irradiations involving dimethylmaleic anhydride is the cyclobutane dimer **50**[96] of dimethylmaleic anhydride.[92] As previously noted, the difference from the behaviour of maleic anhydride is further emphasised by the observation that proton donors such as trifluoroacetic acid produce no acid-catalysis or other effects.[92]

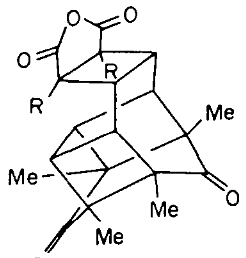
The intramolecular 1,2-addition of an ethylene to a benzene derivative has been observed in the case of the Diels–Alder adduct **51** of cyclopentadiene and 1,4-naphthaquinone, irradiation of which yields **52**.[97] In this case also, the benzene bond undergoing addition clearly must have marked acceptor properties conferred by the two adjacent carbonyl groups: contrast the intramolecular 1,3-cycloaddition of 6-phenylhex-2-enes, to which reference has previously been made.[33]

3.1.6 1,4-*Photoaddition of ethylenes to benzene*: *Photoaddition of allenes*. 1,4-Cycloaddition of simple alkenes to benzene has only been noted in relatively few cases, and is then generally a minor process. For example, the relative quantum efficiencies for the 1,2-, 1,3- and 1,4-cycloadditions of *cis*-but-2-ene to benzene are 6:40:1 respectively,[30] and from cyclobutene and benzene, the 1,3-cycloadduct is formed at 9 times the rate of the 1,4-product.[44] However, allenes do tend to photoadd 1,4- to benzene, and these are the only ethylenes for which this is yet known to be the preferred reaction mode. Thus the major products (**53a** and **53b**) from irradiation of propa-1,2-diene (I.P. 10.16 eV) and cyclonona-1,2-diene respectively in benzene result from 1,4-cycloaddition of one of the allenic ethylenic bonds to benzene.[98] In both cases the corresponding 1,3-adducts **54a** and **54b** are also formed, but with lower quantum efficiencies. In the case of simple ethylenes, it is not yet clear what factors tend to promote 1,4- rather than 1,2-cycloaddition. Thus whereas with the but-2-enes the 1,4-reaction is observed only as a minor process, isobutene, 2-methylbut-2-ene (trimethylethylene), and tetramethylethylene all yield 1,4-"ene" type products **55** together with varying amounts of the 1,2- and 1,3-cycloadducts.[51,60]

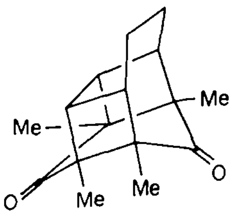
Althouth the 1,4-"ene" process could in principle be concerted, formation of the "ene" product is in practice non-stereospecific, and the ratio of *cis* and *trans* adducts (i.e. **56** and **57** from $C_6D_6$ and tetramethylethylene) is concentration-dependent.[60] Thus thermal *cis*-1,4-dehydrogenation of the "ene"-adducts **56** and **57** formed from a 10% v/v solution of the ethylene in $C_6D_6$ led to the loss of $D_2$ and HD in the ratio 2:7, whereas the corresponding ratio from the adducts formed from a 1% v/v solution was 1:1. Thermal dehydrogenation of such adducts as **55** at 350° yields the aromatic product together with several other compounds, but the product ratio is the same for the adducts from $C_6H_6$ and $C_6D_6$ adducts. This absence of a deuterium isotope effect suggests that the $D_2$:HD ratios provide a correct measure of the ratios of *cis* and *trans* adducts. For the case of tetramethylethylene, (I.P. 8.3 eV) it has been shown that hydrogen is almost certainly transferred to



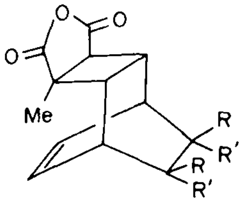
Scheme 4.



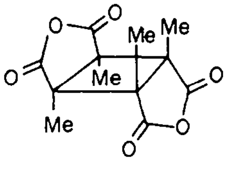
(45) R = H
(49) R = Me



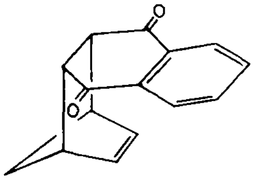
(46)



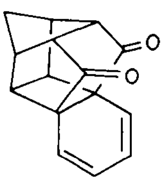
(47) R = R = H
R′–R′ = –CO–O–CO–
(48) R = R′ = CN



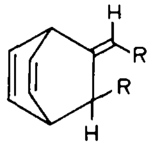
(50)



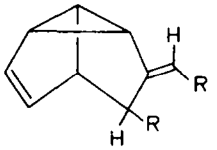
(51)



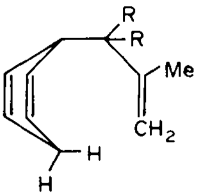
(52)



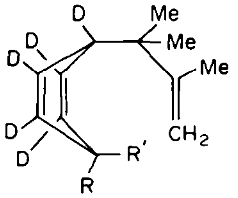
(53) *a*, R = H
*b*, R–R = –(CH$_2$)$_6$–



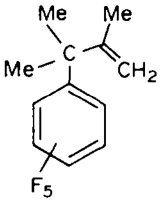
(54) *a*, R = H
*b*, R–R = –(CH$_2$)$_6$–



(55) R = H or Me



(56) R = D, R′ = H
(57) R = H, R′ = D



(59)

the 4-position as a proton rather than as an atom.[60] Thus the rate of formation of "ene" adducts is greatly increased in methanol, whereas acetonitrile is without effect: the use of MeOD leads to specific incorporation of deuterium in the 4-position. These findings are rather surprising in that they demonstrate an essentially polar character for a reaction between two simple hydrocarbons. The proposed mechanism is summarised in Scheme 4. The 1,2-cycloadduct and products of 1,4-addition are postulated to arise via an exciplex of the addends which yields the zwitterion **58**. The "ene"-product has only been observed with 1,1-dimethyl-substituted ethylenes, and the efficiency of the reaction decreases in the series tetramethylethylene > trimethylethylene > isobutene:[51] this is the order of decreasing donor character (I.Ps. 8.3, 8.67 and 9.23 eV respectively) in accordance with Scheme 4. It is pertinent to note here that while *cis*-but-2-ene (I.P. 9.13 eV) does not yield an "ene"-type adduct with benzene both the 1,2- and 1,4-cycloadducts are formed together with the 1,3-product.[30]

In contrast with the benzene case, irradiation of tetramethylethylene in hexafluorobenzene yields no cycloadducts, but **59** and **60** are formed instead. Since HF is evolved during this reaction it is not surprising that neither methanol nor traces of trifluoroacetic acid affect the formation of the product. The formation of **60** may be rationalised in terms of a 1,3 F-shift in the zwitterion **61** analogous to **58**; and elimination of HF from this species would give the product **59**.

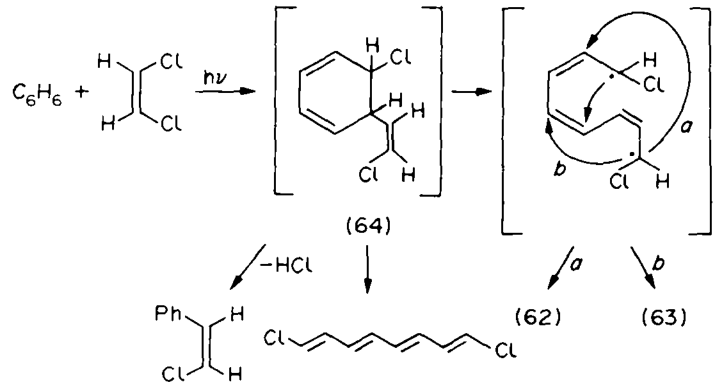
To summarise, ethylenes can undergo 1,2-, 1,3- and 1,4-cycloaddition to the benzene ring, and also 1,4-"ene"-additions. Since orbital symmetry analyses for homopolar processes (absence of charge-transfer effect) predict that only the 1,3-reactor should be allowed as a concerted process, it is rather satisfying that the 1,3-cycloaddition is indeed the major or exclusive process for reactants of closely similar ionisation potentials. The 1,3-cycloadditions are also insensitive to proton donors and solvent polarity effects, as one would expect. On the other hand, 1,2-cycloadditions and 1,4-"ene" additions tend to occur when there is a marked difference in ionisation potentials between the reactants i.e. potential donor–acceptor pairs), and these processes often show marked sensitivity to solvent polarity and proton donors. The cycloaddition reactions are stereospecific in all cases so far examined, but the "ene"-addition is non-stereospecific. The stereospecificity of 1,3-addition evidently results from the availability of at least two allowed concerted pathways. For 1,2- (and perhaps also the little-known 1,4-) cycloadditions it may be that the stereospecificity results from charge correlation (i.e. coulombic interactions) in zwitterionic or other polarised intermediates which prevents the rotation required for loss of stereospecificity. Although there are still some gaps in our knowledge and understanding of these processes, particularly those relating to 1,4-cycloaddition, there is in general a good degree of harmony between theory and experiment.

3.1.7 *Photoaddition of dichloroethylenes to benzene.* Investigations of the photoadditions of *cis*- and *trans*-1,2-dichloroethylenes to benzene have revealed some interesting reaction pathways additional to those described for relatively simple ethylenes in the foregoing section. It was first reported that irradiation of *cis*-dichloroethylene in benzene yields 1,8-dichloro-octa-1,2,3,4-tetraene, but the identification rested only on a UV-spectrum and no products were isolated.[99] A more detailed examination of *cis*- and *trans*-dichloroethylenes in benzene has revealed that the octatetraene is indeed formed, but only as a minor product; six other major reaction products were identified together with the geometric isomer of the dichloroethylene, and hydrogen chloride.[100] The major two of these six products are the *cis*- and *trans*-$\beta$-chlorostyrenes. It is particularly interesting that these are formed with high stereoselectivity at short irradiation times from the corresponding dichloroethylenes. The products of intermediate abundance are two 1:1 adducts **62** and **63** of novel type. Neither of these is believed to be a primary photoproduct. The hypothetical intermediate **64** could account for the results and equally well be the precursor of these adducts, the dichloro-octatetraene, and the two styrenes via the routes shown in Scheme 5, and indeed could account for the stereospecificity in the formation of the styrene. The attempted trapping of **64** using dienophiles has not yet yielded isolable products but the presence of N-phenylmaleimide for example causes corresponding reductions in yields of the two 1:1 adducts and the styrenes, so these may well have a common diene precursor.[48] Both **62** and **63** could also arise in principle via acid-catalysed rearrangement of the 1,3- and/or 1,4-cycloadducts of the dichloroethylenes and benzene (HCl is evolved during the irradiation): precedent exists for the latter rearrangement.[101] The reaction is, however, little affected by acid traps, and the involvement of a 1,3-cycloadduct in the formation of **62** and **63** is considered unlikely as we have found related 1,3-adducts (e.g. **65a** and **65b** from benzene and allyl chloride) to be stable under similar acidic conditions (i.e. HCl evolved during irradiation).[51] Thus we favour adduct **64** as the key intermediate in this process. It is noteworthy that the formation of dichloro-octatetraene in this system is analogous to the much earlier reported production of octa-1,3,5-triene-7-ol from the 254-nm irradiation of a benzene-ethanol rigid matrix at 77K.[102] The minor two products from benzene and dichloroethylenes are cyclobutane dimers of the ethylenes.[100]

In contrast with the above reactions of dichloroethylenes, the irradiation of dichlorovinylene carbonate in benzene yields phenylchlorovinylene carbonate and 1:1, 2:1 and 2:2 adducts.[65,103] The reactive species for formation of the 1:1 adducts is deduced to be the triplet addend (cf. maleimide addition).[65] Thus the cycloadditions are formally symmetry-allowed as concerted processes: but whether the triplet reactions will in practice follow a concerted pathway remains a moot point.[15] The 1:1 *exo*-1,2-cycloadduct **66** has been isolated, but from the stereochemistry of the secondary reaction products (i.e. the 2:1 adducts) and their probable mode of formation, the *endo*-isomer **67** has been inferred to be an intermediate.[65] The 2:1 adducts **68**, **69** and **70** are formed by attack of triplet excited dichlorovinylene carbonate on **66** and **67**, but the 2:2 adducts have been suggested to arise from the dimerisation of the diradical 1:1 adduct precursor **71**. This system should also be compared with that of benzene-vinylene carbonate from which 1,3- and 1,4- 1:1 cycloadducts are reported (Section 3.1.2).[53]

### 3.2 *The photoaddition of acetylenes to benzene*

This process has provided an important and convenient synthetic route to cyclo-octatetraenes, and indeed the only direct route from benzenes to cyclo-octatetraenes. We may first note that the orbital symmetry aspects of the addition reactions of acetylenes to benzenes are the same as those for ethylenes.[15] Thus the 1,3-cycloaddition would be a symmetry allowed concerted process from $S_1$ or $T_1$ excited acetylene plus $S_0$ benzene or $S_1(B_{2u})$ benzene plus $S_0$ acetylene, and

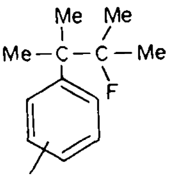


Scheme 5.

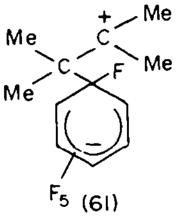
the 1,2- and 1,4-concerted processes would be symmetry allowed from $S_1(^1B_{1u})$ or $T_1(^3B_{1u})$ benzene plus $S_0$ acetylene. Likewise, mixing with charge-transfer states, as in donor-acceptor systems, would be expected to promote 1,2- and 1,4-cycloadditions. As maleic anhydride was originally proposed, and subsequently confirmed, to undergo an initial 1,2-cycloaddition to benzene, it was reasoned that the analogous addition of an acetylene should yield a bicyclo[4.2.0]octatriene which would undergo valence bond isomerisation to the corresponding cyclo-octatetraene. This expected reaction sequence was confirmed to occur in practice.[104,105] Thus irradiation of dimethyl acetylenedicarboxylate in benzene gave dimethyl cyclo-octatetraene-1,2-dicarboxylate (**72**) as essentially the sole product. Proof of the structures was made by comparison with authentic cyclo-octatetraenes,[105] and the reaction has been extended to other acetylenes.[34,105,106] Further studies have shown that the formation of the product proceeds via a mechanism partly similar to that described in Section 3.1.3 for the maleic anhydride addition in that a polarised species, e.g. **73**, is involved as an intermediate: in the presence of a proton donor this is intercepted to give dimethyl phenylfumarate and -phenylmaleate at the expense of the cyclo-octatetraene.[81] The polar intermediate **73** also collapses to the bicyclic triene (**74**) which rearranges to the cyclo-octatetraene (**72**)† or can be trapped by tetracyanoethylene as the 1:1:1 adduct **75** (Scheme 6).[34] A point of distinction from the maleic

---

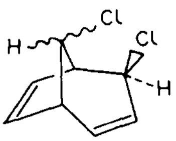
†It has been shown that the cyclo-octatetraene (**72**) has the structure shown in which a single bond is located between the substituents: the usual rapid bond exchange between "Kekulé" forms does not occur in this case, probably for steric reasons. Models indicate a dihedral angle of *ca.* 70° between the substituents. The corresponding dicarboxylic acid is markedly resistant towards formation of a conventional cyclic anhydride (**72a**).[107]



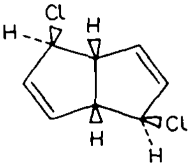
(60)



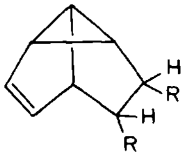
(61)



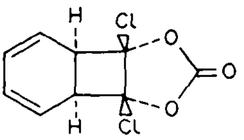
(62)



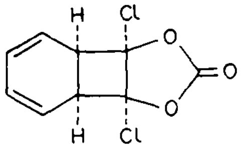
(63)



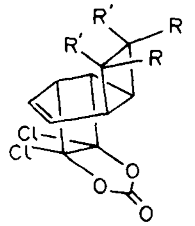
(65) *a*, R = CH$_2$Cl, R′ = H
*b*, R = H, R′ = CH$_2$Cl



(66)

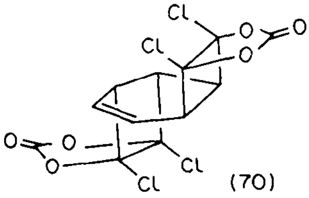


(67)

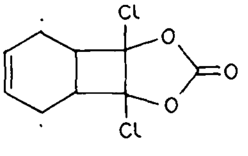


(68) $R = Cl, R'–R' = –O–\overset{O}{\overset{\|}{C}}–O–$

(69) $R–R = –O–\overset{O}{\overset{\|}{C}}–O–, R' = Cl$

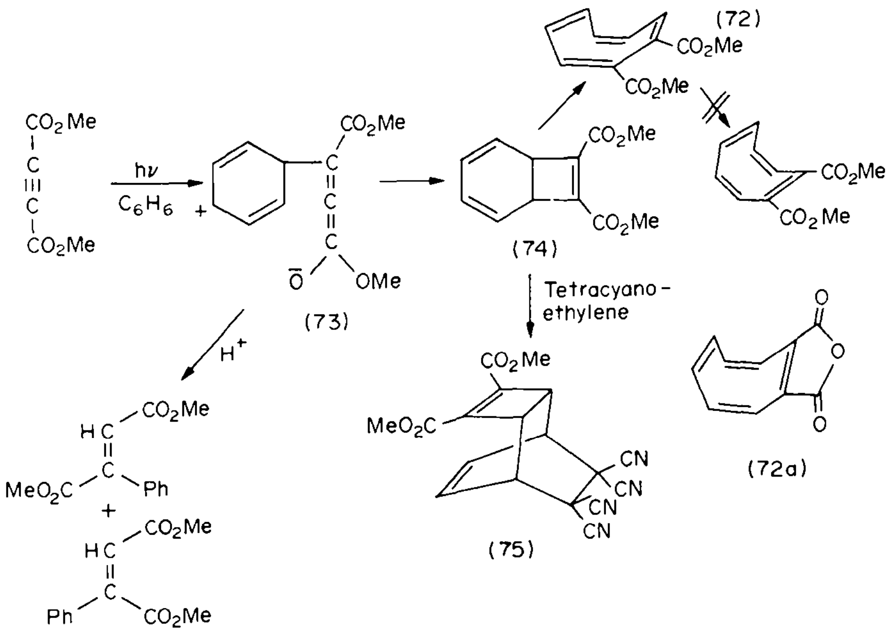


(70)

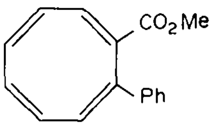


(71)

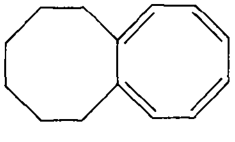
anhydride addition is that the reaction of acetylenes does not involve charge-transfer excitation: indeed, solutions of acetylenes in benzene—even potentially acceptor acetylenes such as dimethyl acetylenedicarboxylate—show no observable charge-transfer absorption. (This feature is somewhat surprising in view of the general greater reactivity of acetylenes than corresponding ethylenes towards nucleophiles, and the lower reactivity towards electrophiles). From an investigation of the photoaddition of methyl phenylpropiolate to benzene to give the cyclo-octatetraene (**76**), it appears that the excited species responsible for the reaction is the acetylene, not the benzene, in accordance with predictions from the orbital symmetry analysis (i.e. allowed as a concerted process from $S_1$ acetylene plus $S_0$ benzene, but not from $S_0$ acetylene plus $S_1$ benzene).[34] The effects of proton donors mentioned above suggest that charge-transfer occurs *after* excitation of the acetylene (i.e. exciplex formation). However, in the case of 1,2-addition of cyclo-octyne to benzene it has been proposed from quenching data that the acetylene is in the triplet state. This reaction is somewhat atypical in that formation of the cyclo-octatetraene (**77**) is reported to occur with remarkably high efficiency (at 66% conversion, 56% yield).[108] Pending further studies, it would be premature to conclude from this work with cyclo-octyne that the reactions involving other less strained acetylenes also occur *via* triplet species. Indeed it has recently been shown that the corresponding intramolecular acetylene-benzene addition of 6-phenylhex-2-yne to give 2-methyl bicyclo [6,3,0] undeca-1,3,5,7 tetraene (**78**)[109] is significantly retarded by xenon, so this is evidently a singlet process.[110] It is also worth noting that ionisation potential differences between the addends could again be important, as with ethylenes; but this aspect of the reaction has not been systematically examined. That the formation of parent cyclo-octatetraene from benzene and acetylene does not involve tetramerisation of the ace-



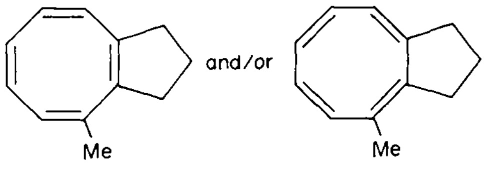
Scheme 6.



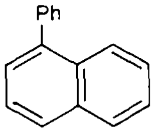
(76)



(77)



(78)

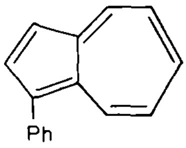


(79)

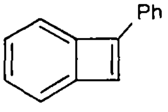
tylene has been shown by the formation of 1,2,3,4,5,6-hexadeuteriocyclo-octatetraene from the irradiation of acetylene in $C_6D_6$.[34]

It is interesting that irradiation of phenylacetylene[111] and diphenylacetylene[112] in benzene yields the corresponding phenylnaphthalenes and -azulenes, (e.g. **79** and **80** from phenylacetylene) as dimers of the acetylene, together with the expected phenylcyclo-octatetraenes. Recent work with diphenylacetylene, has indicated that the reaction may proceed via the $T_1$ acetylene to give initially a labile isomer of the acetylene, probably phenylbenzocyclobutadiene (**81**), which dimerises to the observed products.[113] The formation of **81** would represent an extremely surprising intramolecular addition of acetylene to the benzene ring. A rather more orthodox example of this latter process has been provided by the irradiation of 6-phenylhex-2-yne, as mentioned earlier.[109]

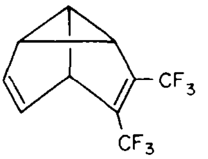
All the above additions of acetylenes appear to involve 1,2-addition to the benzene ring. There are indeed surprisingly few reported cases in which an acetylene undergoes 1,3-photoaddition to a benzene ring to give a semibullvalene. Perfluorobut-2-yne was reported to undergo addition to benzene to yield the three isomeric semibullvalenes (**82**, **83** and **84**), together with the corresponding substituted cyclo-octatetraene.[114] Of these three isomers, only **82** could be formed by direct addition. We also note that the ratios of these isomers were very similar to those previously reported for photosensitised isomerisation of the known thermal 1,4-cycloadduct (**85**);[115] so it seems probable that they were all derived as secondary photoproducts from the thermal adduct **82**, and that little or no direct 1,3-addition of the acetylene to benzene actually occurred. On the other hand 1,3-cycloaddition of diphenylacetylene to triethyl trimesate does appear to occur, but the reaction requires several days' irradiation, and the adduct **86** has only been obtained in an impure state in low yield.[116] The possibility of an intermediate 1,4-adduct in this case may be discounted by the lack of products which bear phenyl groups other than in the expected positions. This addition reaction is all the more interesting as 1,3-addition was not observed in previous work with trimethyl trimesate and *cis*-cyclo-octene.[117] The major reactions in this case involved 1,2-cycloaddition to give three isomers of the tetracyclo[6.6.0.0$^{2,7}$.0$^{3,6}$]tetradec-4-ene system (**87**). A 1,3-cycloadduct **88** has also been reported to be present among the reaction products from the irradiation of naphthalene in the presence of dimethyl acetylenedicarboxylate.[118]



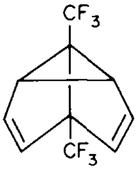
(80)



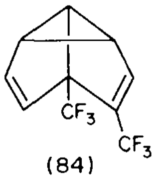
(81)



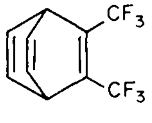
(82)



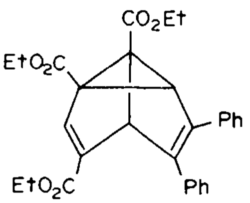
(83)



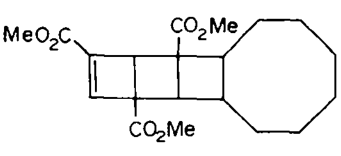
(84)



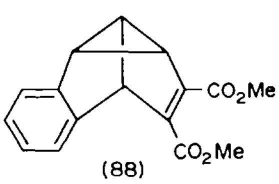
(85)



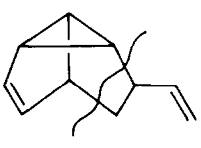
(86)



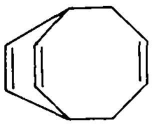
(87)



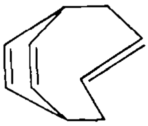
(88)



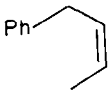
(89)



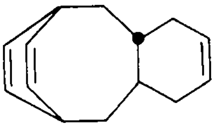
(90)



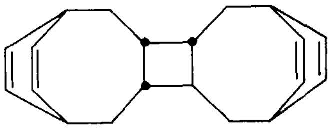
(91)



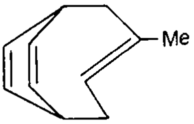
(92)



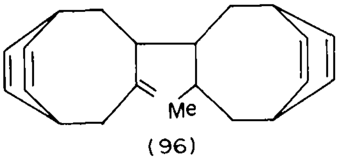
(93)



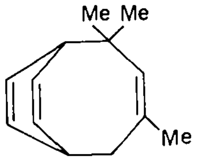
(94)



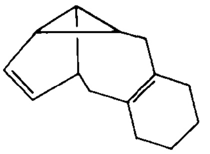
(95)



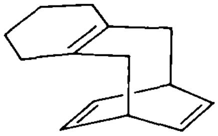
(96)



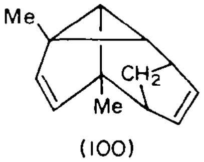
(97)



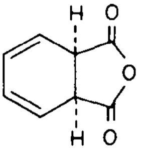
(98)



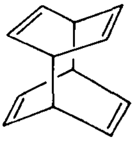
(99)



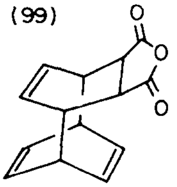
(100)



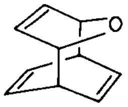
(101)



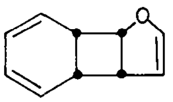
(102)



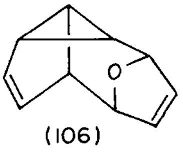
(103)



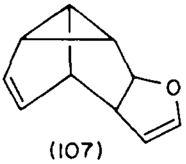
(104)



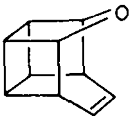
(105)



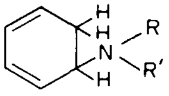
(106)



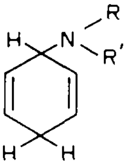
(107)



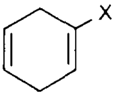
(108)



(109) a, R = alkyl, R' = H
b, R = R' = alkyl



(110) a, R = alkyl, R' = H
b, R = R' = alkyl



(111)

### 3.3 *Photoaddition of* 1,3-*dienes to benzene* (*see Section* 3.1.6 *for* 1,2-*dienes*)

The photoaddition of 1,3-dienes to benzene was first described by Koltzenburg and Kraft in two reports, the first of which was concerned principally with the systems butadiene-benzene and isoprene-benzene, and the second with other benzenoid compounds and 1,3-dienes.[119] Buta-1,3-diene yields the 1,2-/1',3' adduct (**89**) and the *cis*- and *trans*-1,4-/1',4'-cycloadducts (**90** and **91**) together with the substitution product (**92**). The *trans*-1,4-adduct **91** undergoes further addition of the diene to give the 1 : 2 adduct **93** and yields the cyclobutane dimer **94** apparently via a symmetry-allowed suprafacial-antarafacial thermal addition. The corresponding adduct **95** from isoprene dimerizes to **96** via an ene-reaction. It is worthy of note that the formation of **91** and **95** provides the only known examples in which 1,3-dienes undergo cycloaddition in their *transoid* conformation. $S_1$ benzene is considered to be the reactive excited species in the primary 1′,4′ and 1′,3′ addition reactions. The orbital symmetry diagrams for 1,4-cycloaddition of the *cisoid* and *transoid* conformers of butadiene are presented in Figs. 5 and 6 respectively. It will be seen from this analysis that the diene should add more readily in its *transoid* than in its *cisoid* conformation. Indeed from a quoted experiment[120] the ratio of **90** to **91** is 5:67; but under these conditions there is of course a considerable preponderance of the *transoid* conformer of the diene. The orbital symmetry analysis in the *transoid* case may be less rigorous than usual as the symmetry axis does not pass through a benzene bond (Fig. 6). Since the energy of $S_1$ butadiene > $S_1$ benzene, non-Hückel levels are used for butadiene in Figs. 5 and 6 (see Part I).[1]

The photoaddition of buta-1,3-diene to benzene has been carried out in the presence of iodine under which conditions the very reactive 1,4*trans* adduct **91** is converted into the less-strained *cis*-isomer **90**: and this latter compound is thereby formed in useful amounts.[121] Since the early reports by Koltzenburg and Kraft, several other groups have studied the process principally with substituted naphthalenes and anthracenes using various dienes including cyclopentadiene,[122] cyclohexa-1,3-diene[122–127] and cycloheptatriene.[128,129] Some of the earlier work with benzene and 2,3-dimethylbuta-1,3-diene and s-*cisoid* 2,4-dimethylpenta-1,3-diene has also been reinvestigated particularly in the light of work on the addition of dienes to naphthalene and anthracene which has suggested that the ground-state conformations of the dienes could determine the adduct structure and that the s-*cisoid* conformation would be more reactive than the *transoid*.[123,124] Indeed the s-*cisoid* diene and benzene gave 37% of the 1,4-/1′,4′-adduct **97** and 21% of a complex mixture of 1,3-adducts, whereas 2,3-dimethylbutadiene yielded an extremely complex mixture of products which included cycloadducts, substitution products, and diene dimers as well as "high molecular weight material".[130] It is interesting that preliminary studies with the s-*cisoid* diene and toluene and benzonitrile indicate that acceptor substituents direct addition to substituted positions (as with benzonitrile and ethylenes[61]) whereas donor groups assist reaction at the most remote unsubstituted sites (as with methylbenzenes and maleic anhydride[82]). The use of acyclic dienes is always beset by diene isomerisation problems and subsequent side reactions. Such problems have been avoided by use of the two conformationally fixed 1,3-dienes 1,2-dimethylenecyclohexane and 3-methylenecyclohexene.[131] The former diene gave only the two primary photoadducts (**98** and **99**) in a 1:2 ratio by way of 1,3-/1′,4′- and 1,4-/1′,4′-modes of cycloaddition respectively. In contrast, the rigid *trans*-diene 3-methylenecyclohexene gave very low yields of a complex mixture of products. While these results are in accord with one earlier suggestion concerning the reactivity of *cisoid* and *transoid* diene conformers,[130] it is of course pertinent that the 1,4-/1′,4′-adduct from 3-methylenecyclohexene and benzene would be considerably strained. It is worthy of note that the hitherto unknown 1,3-/1′,4′-cycloaddition of a *cisoid* 1,3-diene had earlier been predicted to be an allowed concerted process from either $S_1$ diene and $S_0$ benzene or $S_1$ benzene and $S_0$ diene.[15] Although cyclopentadiene has been reported not to undergo cycloaddition to benzene,[120] 1:1 adducts of unknown structure are now known to be formed in very low yield.[132] On the other hand, the photoaddition of this diene to xylenes does seem to give isolable amounts of products, the major of which is reported to be the 1,3-/1′,4′-cycloadduct **100**.[133]

As noted in Section 2, no photo-dimers of benzene have yet been obtained directly from benzene. The light-induced 1,4-cycloaddition of 1,2-dihydrophthalic anhydride (**101**) to benzene might provide an attractive indirect route to the elusive 1,4-/1′,4′-dimer (**102**). Yang *et al.* have recently reported the formation of **103** in a crude yield of 13% from the irradiation of benzene solutions of the rigid *cis*-diene **101**.[134] We now look forward to the synthesis of **102** by oxidative decarboxylation of **103**.

The photoaddition of furan to benzene provides the first example of light-induced cycloaddition of two monocyclic aromatic systems, but has been described in two seemingly conflicting independent reports.[132,133] The authors subsequently published a joint report which substantially clarified the situation.[135] It transpired that most of the apparent discrepancies in the two earlier reports arose from experimental differences, especially in the irradiation sources. It is now agreed that irradiation of 1:1 benzene-furan mixtures with a low intensity low pressure mercury arc (substantially at 254 nm) yields the 1,4-/2′,5′-adduct **104** as the major primary product, as reported in Ref. 132. This adduct yields the Cope-rearranged 1,2-/2′,3′-isomer **105** both photochemically and thermally: it also undergoes benzene-sensitized decomposition to starting materials, as does its Cope isomer **105**.[132] On the other hand, irradiation of this system with a high-intensity medium-pressure lamp (which emits over a much broader range of wavelengths than do low-pressure lamps), and/or the use of high temperatures in the work-up and isolation procedures, effectively destroys large amounts of these adducts **104** and **105**. Thus the photochemically and thermally more stable minor components from the irradiation, viz. the 1,3-/2′,5′-adduct **106**, the 1,3-/2′,3′-adduct **107**, and the cage isomer **108** of **104**, become the apparent major products.[133] The only aspect of this system in some dispute is the quantum efficiency of the primary photoprocess.

Although pyrrole readily undergoes photoaddition to benzene, the process is totally different from those which we have described for furan and dienes and is more relevantly considered in the next Section which deals with the photoaddition of amines to benzene. Thiophen shows no tendency to form adducts with benzene or indeed any other aromatic compound yet studied.[136]

### 3.4 *The photoaddition of aliphatic amines, pyrroles, and ether to benzene*: *reductive photoamination of benzene*

The photoaddition of amines to benzene is a very general process first reported in 1967 for primary and secondary aliphatic amines[137] and pyrrole.[138] The reaction has subsequently been shown to occur with tertiary aliphatic amines in the presence of a proton donor,[139] and has been extended to other aromatic systems (see, e.g. Refs. 140–143). The reaction is of synthetic significance since the resulting substituted cyclohexa-1,4-dienes are not readily available by other routes, and although quantum yields are generally low (*ca.* 0.005,[144] but *ca.* 0.2 with pyrrole[48]), gram quantities of the major products can usually be obtained without difficulty: see also Section 5.[145]

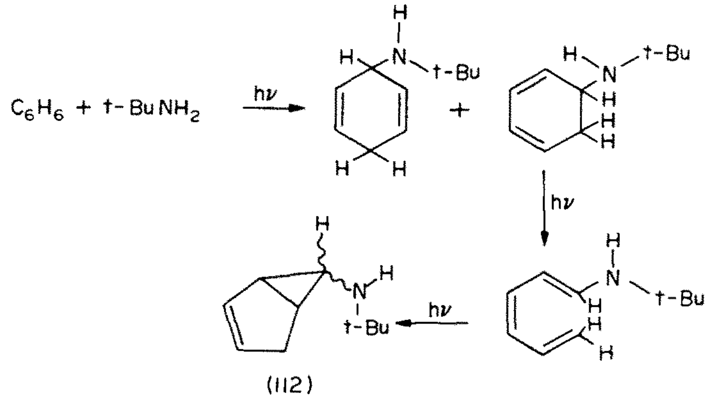
Primary and secondary aliphatic amines yield the 1:1 photoadducts **109** and **110** by 1,2- and 1,4-acyclic addition respectively of the N–H bond across the benzene ring.[137,146]† The 1,4-adducts normally predominate, and are fairly photo-stable. On the other hand, the 1,2-adducts from primary amines are photo-labile and undergo a light-induced sequence of reactions (Scheme 7) to give the formal 1,3-benzene-amine adduct, e.g. **112**.[146] It is not believed that 1,3-adducts of type **112** arise by direct addition to the ring (contrast 1,3-addition of alkenes already discussed in Section 3.1.1), or by addition to benzvalene (as with methanol, etc. as discussed in Part I[1]). Surprisingly, the corresponding 1,2-adducts **109b** from the secondary amines are essentially photostable so the relative proportions of the 1,2- and 1,4-photoproducts from secondary amines and benzene are only dependent on the particular amine, and no 1,3-products analogous to **112** are formed. In contrast, the only photo-adduct **113** from tertiary aliphatic amines and benzene is that produced by attack at the α-methylene group and again involves the 1,4-aromatic positions.[139] In all these reactions small amounts of the benzene-reduction products cyclohexa-1,4-diene and 1,1',4,4'-tetrahydrobiphenyl **114** are formed.

Much has been written concerning both the physical and chemical aspects of the interactions of amines with singlet excited aromatic compounds (see, e.g. Refs. 137–143, and 146–150). Such interactions in non-polar media are currently considered to involve the initial formation of an "encounter complex" which leads to an electronically excited charge-transfer complex or an exciplex.[150] Emission attributed to the exciplex has been observed in many irradiated arene-amine systems, but the intensity and and lifetime of this fluorescence tend to decrease with increased solvent polarity.[151] Flash photolysis studies have indicated that this quenching process is associated with the formation of radical-anions and radical-cations of the acceptor and donor molecules.[152,153] The phenomenon is accounted for by a scheme in which formation of the fluorescent exciplex from the encounter complex is impeded and its lifetime reduced by processes in which the encounter complex and the exciplex yield a highly solvated ion-pair which may dissociate to the solvent-separated ions.[152]

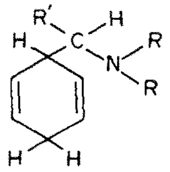
In the absence of sufficient photophysical studies on

---

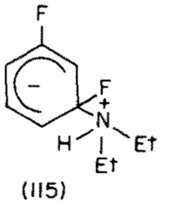
†In contrast, Birch reduction of substituted benzenes $C_6H_5X$ normally gives dienes of type **111** as major products.



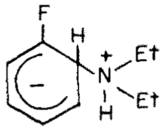
Scheme 7



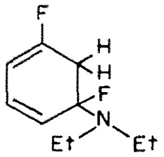
(113)



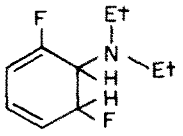
(115)



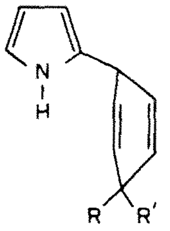
(116)



(117)



(118)



(119) R=R'=H (120) R=D, R'=H
(121) R=H, R'=D

the benzene-amine systems (e.g. exciplex emission data) we do not feel it profitable to speculate at length on the fine details of the mechanism; but the various steps involved are probably essentially restricted to proton transfer, one-electron transfer, or two-electron transfer in encounter complexes and/or exciplexes.[137–143,146–150,154] It has however been shown that all the aliphatic amines (primary, secondary, and tertiary amines and pyrroles) which photoadd to benzene also quench benzene fluorescence in hydrocarbon solvents at a diffusion-controlled rate.[155,156] The efficiency of the photoaddition reaction is extremely low for tertiary amines unless a proton donor such as methanol or water is present. The observation that 5% of the proton donor is as effective as 30% indicates that its promoting effect does not depend on solvent polarity changes.[145] Primary and secondary aliphatic amines can presumably function as their own proton donors, and incorporation of methanol or other polar solvents has a detrimental effect on the efficiency of the additions.[144] These differing solvent effects indicate differences in mechanistic detail for the addition of primary and secondary amines on the one hand and tertiary amines on the other. With both types of process, a proton source is clearly essential and with tertiary amines proton transfer appears to be the chemical rate-determining step. The mechanism in Scheme 8 accounts satisfactorily for the fluorescence quenching and reaction products observed in the case of triethylamine and benzene.

This mechanism resembles that of the thermal Birch reduction in that it involves electron transfer to the benzene. Thus sodium in liquid ammonia provides an electron-donor system sufficiently strong to transfer an electron to $S_0$ benzene, whereas the stronger electron acceptor $S_1$ benzene is required for electron transfer from amines. The mechanistic relationship between reductive photoamination and the Birch reduction is further illustrated by the production of small quantities of cyclohexa-1,4-diene and the radical combination product 1,4-, 1′,4′-tetrahydrobiphenyl **114**: the ratios of photoadducts from triethylamine and benzene to these neutral products are the same in the absence and presence of methanol or other proton donors.[145] Production of cyclohexa-1,4-diene in this manner provides the only known example of the photoreduction of benzene, and formally constitutes a type of photo-Birch reduction (see also Ref. 142). Small amounts of N,N-dialkylanilines are also produced in the reactions of secondary amines, e.g. diethylamine: the formation of such products appears to provide a rare example of photonucleophilic substitution in benzene itself.[155]

As yet there have been no reports concerning the photoaddition of aromatic amines to benzene, but since such reactions are known with anthracene[143] where the aromatic compound can be selectively excited, the former processes might possibly occur under experimental conditions which permit significant excitation of the benzene; but one would not expect them to be very efficient. They certainly do not occur to any significant extent under the conditions used for the addition of aliphatic amines.[155]

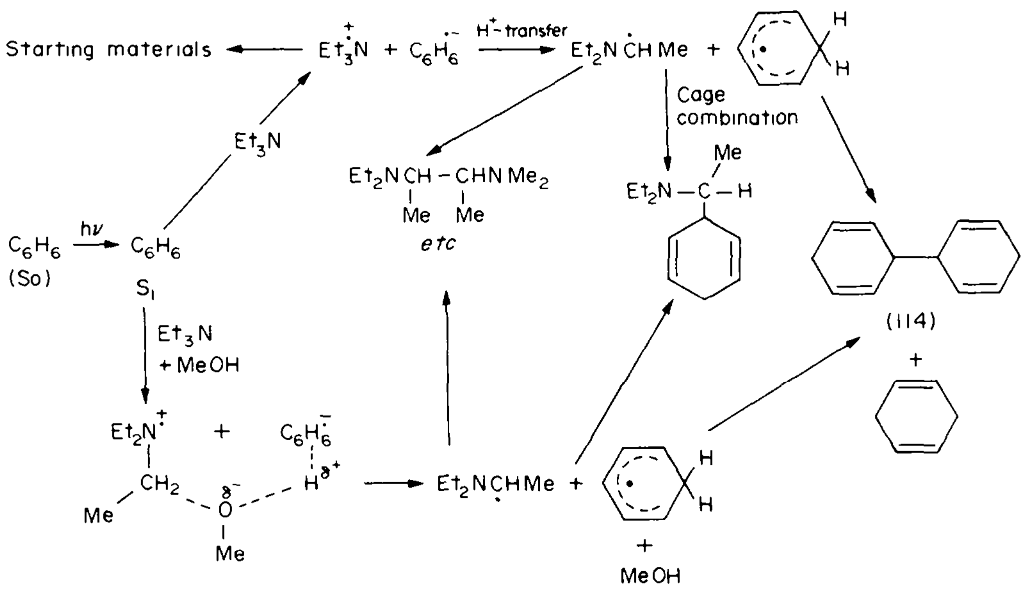
3.4.1 *Photoreactions of amines with substituted benzenes: photochemical cine-substitution.* Photoadducts are also formed between amines and some substituted benzenes: a study of mono- and di-fluorobenzenes has provided some particularly interesting results.[154] As noted in Section 3.4, only in the case of the addition of tertiary amines to benzene is the reaction promoted by methanol, and the corresponding additions of primary and secondary amines are actually inhibited by methanol. Methanol similarly inhibits the reactions of primary and secondary aliphatic amines with mono-and di-fluorobenzenes, and chemical yields of the addition and substitution products from these arenes decrease with increase in solvent dielectric constant (cyclohexane, ether, acetonitrile, methanol). Although free-radical derived products, e.g. fluorinated tetrahydrobiphenyls analogous to **114** are also formed, their proportions relative to the adducts and substitution products decrease in the series benzene, fluorobenzene and difluorobenzenes, but the overall chemical yields of photoadducts increase markedly in the same order. The fluorobenzenes yield several adducts from primary and secondary amines, but with monofluorobenzene and *o*- and *m*-difluorobenzenes, the major adducts from both primary and secondary amines reflect "*ortho*" addition of N–H whereas that from *p*-difluorobenzene results from a "*para*" addition. All the fluorobenzenes give the expected "normal" substitution products with such amines, but it is most interesting that cine-substitution also occurs with the difluorobenzenes. The major involvement of arynes in this latter process has been discounted by the absence of effects of benzyne traps and by the predominance of the "normal"-over the cine-substitution products. Thus we have suggested that the substitution arises mainly by an addition–elimination mechanism involving either Wheland-type intermediates (e.g. **115** and **116**) or unstable (undetected) chemical adducts (e.g. **117** and **118**). The incorporation of deuterium into the photochemical products from the irradiation of the fluorobenzenes with $Et_2ND$ is significant. Thus while the adducts have $>0.85$ atoms of deuterium, as expected, the "normal"-and cine-substitution products incorporate 0.5–0.6 and 0.3–0.4 atoms respectively. The N,N-diethylaniline formed from the irradiation of $Et_2ND$ with fluorobenzene also contained 0.45 atoms of deuterium. Such deuterium incorporation in the substitution products supports the proposed addition-elimination mechanism for their formation.[154]†

The results with fluorobenzenes shed some light on the corresponding benzene reactions. The differing solvent polarity effects suggest that the photoreaction of tertiary amines with benzene involves a relatively non-polar excited complex, and 1-electron transfer followed by a rate determining proton transfer (Scheme 8), whereas the reaction with secondary and primary amines proceeds from a more polar exciplex which shows a tendency to be quenched by polar solvents. The formation of an even more polar excited complex with the more strongly electron-accepting fluorinated benzenes would explain why the corresponding photoadditions are more strongly inhibited by polar solvents. In this latter case, the excited complex evidently reacts only in part by the 1-electron/proton transfer route to give free radicals, and to a far greater extent by a 2-electron transfer process to yield intermediates of Wheland-type (**115** and **116**).

3.4.2 *Photoaddition of pyrroles to benzenes.* The photoreactions of pyrroles with benzenes and the factors which affect the reactions are somewhat analogous to

---

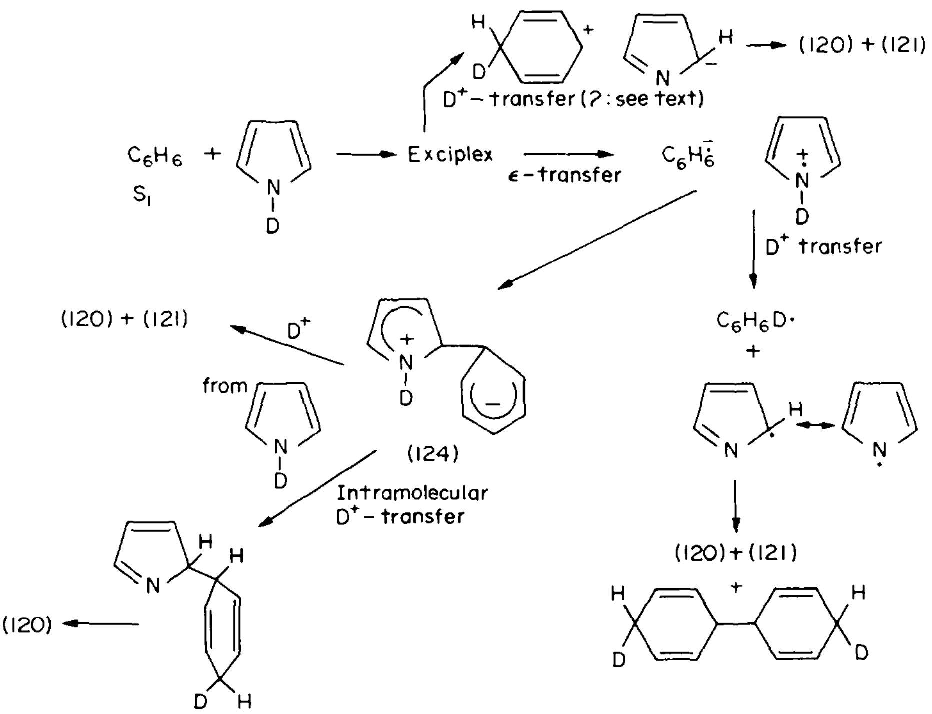
†This mechanism may not apply more generally in photonucleophilic substitution. Thus Professor Havinga has kindly informed us that photochemical methoxy exchange with *m*-nitroanisole in $^{14}CH_3O^-/^{14}CH_3OD$ does not lead to incorporation of deuterium.



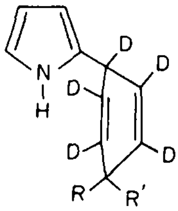
Scheme 8. Photoaddition of triethylamine to benzene.

those described above for amines. But the major product (*ca.* 80%) **119** from the irradiation of pyrrole in benzene solution more resembles that from tertiary amines in its structure than that from secondary amines, in that reaction occurs at carbon rather than nitrogen.[79,138,145] But as with secondary amines, the reaction proceeds at a slower rate in polar solvents.[48]

The stereoselectivity of the benzene-pyrrole reaction has been examined by irradiation of the systems benzene/N-deuteriopyrrole and hexadeuteriobenzene/pyrrole.[79,139,145] The adducts bearing deuterium and hydrogen at the 4-position constitute at least 80% of the reaction mixtures: the former process gave a 4:1 ratio of the adducts **120** and **121**, and the adducts **122** and **123** from the latter system were formed in a 3:2 ratio. The modest predominance of adducts **120** and **122** suggests that intra- and intermolecular proton transfer occur concurrently, as shown in Scheme 9. Direct proton-transfer within the exciplex is shown as a possibility, but is not likely to make a major contribution since it does not seem to occur in related systems, e.g. methanol–benzene and would not account for the "free-radical" products.



Scheme 9. Photoaddition of N-deuteriopyrrole to benzene.



(122) R = H, R′ = D
(123) R = D, R′ = H

Pyrrole quenches the fluorescence of benzene[156] and naphthalene (to which it also adds[149]) at a diffusion-controlled rate. The mechanism of the photoaddition of pyrrole to benzene summarised in Scheme 9 is consistent with all the observed facts, but as little is known of the photophysics of the process we again have not felt justified in speculating on the possible involvement of encounter complexes and/or exciplexes. The reaction shows a modest degree of stereoselectivity, but because tetrahydrobiphenyl is also produced in the process, a mechanism involving combination of the radical-anion radical-cation pair to yield the zwitterionic intermediate **124** cannot be the sole pathway involved. Proton transfer to form radicals evidently occurs to some extent, followed by radical combination within and outside the solvent cage. However the degree of stereoselectivity observed is difficult to reconcile with an exclusive radical pathway.

It is consistent with the mechanism outlined in Scheme 9 that no significant photoreaction is observed between N-methylpyrrole and benzene; but in the presence of a proton donor such as methanol, 2- and 3-cyclohexa-2′,5′-dienylpyrroles **125** and **126** are obtained.[145] The use of MeOD as solvent yields the same two products with deuterium in the 4′-position. The photoreaction with pyrrole has been extended to alkylbenzenes. Toluene for example gives a 2:3 mixture of the major adducts **127** and **128**, but no products derived from benzyl radicals.[79]

3.4.3 *Intramolecular photoadditions of amines to the benzene ring.* Intramolecular analogues of the tertiary amine-benzene addition have been investigated with compounds of type $Ph(CH_2)_nNMe_2$.[157] Compounds in which n = 2, 3 and 4 all display broad long-wavelength emission in the 290–360 nm region (see Fig. 8): this is at a maximum with n = 3 and is assigned to the fluorescence from an intramolecular exciplex of charge-transfer character resulting from interaction of the $S_1$ phenyl group with the tertiary amine function.[158] Intramolecular photocyclisation occurs more readily when n = 3 than when n = 4, and no such reaction has been detected when n = 1 or 2. It is interesting that cyclisation occurs at a *meta* position: thus $Ph(CH_2)_3NMe_2$ gives the product **129**, and $Ph(CH_2)_4NMe_2$ correspondingly gives **130**. Inspection of molecular models of the starting materials shows that there is a maximum orbital overlap between the phenyl ring and the nitrogen lone pair for n = 3 and 4, when the nitrogen atom can reside over an *ortho* position in the ring thereby bringing the N-methyl group over a *meta*-position. These intramolecular cyclisations offer the interesting possibility of a new approach to the synthesis of heterocyclic species related to the morphine alkaloids.

3.4.4 *The photoaddition of diethyl ether to benzene.* A superficially similar type of process to that observed with the tertiary amines also occurs on irradiation of diethyl ether and benzene in the presence of trifluoroacetic acid to give the adduct **131**.[159] In this case, however, the reaction only proceeds in the presence of trifluoroacetic acid, and the weaker proton donor methanol is without effect. These observations suggest involvement of the benzenonium ion $C_6H_7^+$ which can be formed from benzene and trifluoroacetic acid but not from benzene and methanol. Thus unlike the amine-benzene photoaddition reactions, addition of diethyl ether appears to require protonation of the aromatic ring prior to electronic excitation. The addition of ether further differed from addition of amines in that it gave no cyclohexa-1,4-diene and tetrahydrobiphenyl as by-products: free radical intermediates therefore appear not to be involved. It has been suggested that electron transfer from unprotonated ether to a photoexcited $C_6H_7^+$ species produces the intermediate **132** which then undergoes deprotonation and rearrangement to adduct **131**. An intermediate analogous to **132** has recently been suggested for the photosubstitution of CN in tetracyanobenzene[160a] and halogen in halogenated phthalonitriles.[160b] each by tetrahydrofuran.

### 3.5 *Photoadditions to polycyclic and heterocyclic aromatic systems*

Although the photoreactions of polycyclic and heterocyclic aromatic systems are beyond the scope of this review, the reader should note that many of the photoaddition reactions which we have described for the benzene ring also occur with naphthalene, phenanthrene, anthracene, and their simple derivatives.[3] Additions of maleic anhydride provide an exception to this generalisation. Benzene forms the 2:1 photoadduct **38a** as we have described, but naphthalene forms no photoadduct with maleic anhydride.[161] Phenanthrene forms the 9,10-photoadduct **133**,[162,163] whereas the effect of irradiating solutions containing anthracene and maleic anhydride is merely to accelerate the known Diels–Alder reaction.[164]

Relatively few examples of photoaddition to heterocyclic aromatic systems are known, although the addition of furan to benzene has been described in Section 3.3 and thiophen is reported to yield photocycloadducts with dimethyl acetylenedicarboxylate,[165] maleic anhydride, and maleimides.[166] On the other hand the photochemistry of pyridine, quinoline etc. tends to be dominated by substitution processes.[167] The reader wishing to investigate this rather neglected area should consult Ref. 167 and the Annual volumes 1–8 of *Phochemistry.*[3]

## 4. PHOTOSUBSTITUTION REACTIONS OF BENZENE

Over the years there have appeared numerous accounts of light-induced substitution (particularly nucleophilic substitution) into substituted benzenes and naphthalenes. For a general discussion of photonucleophilic substitution the reader is referred elsewhere.[2,3] Here we restrict ourselves to *photoelectrophilic substitution* reactions of hydrogen atoms on the benzene ring. Many, but not all, are substitutive addition processes (e.g. maleic anhydride + benzene $\xrightarrow[h\nu]{H^+}$ phenylsuccinic anhydride: see also Sections 3.1.3).

In several of the foregoing cyclic and acyclic addition reactions, proton donors have been added either as a mechanistic probe, for example in the addition of maleic anhydride,[81] or to facilitate a step in the reaction pathway, for example in the addition of tertiary aliphatic amines.[139] Trifluoroacetic acid has been used as a strong proton donor in a number of these systems, being reasonably photostable. It does however undergo an interesting photoreaction with benzene to form $\alpha,\alpha,\alpha$-trifluoroacetophenone as an initial product.[168]† Secondary products of this reaction were the pinacol **134** and 2,2,2,-trifluoro-1,1-diphenylethanol **135**, and several minor products including biphenyl were also produced. Although the UV absorption spectrum of mixtures of benzene and trifluoroacetic acid indicates the possible presence of the benzenonium ion, it is difficult to involve this species in a mechanism which accounts adequately for formation of the trifluoroacetophenone.

The results are more consistent with charge-transfer from unprotonated $S_1$ benzene to trifluoroacetic acid to give a spin-coupled radical-ion pair, or a polarised exciplex, which transforms into the zwitterionic intermediate **136** *en route* to $\alpha,\alpha,\alpha$-trifluoroacetophenone. The 2,2,2-trifluoro-1,1-diphenylethanol **135** arises via a novel acid-catalysed (methanol or trifluoroacetic acid) secondary photoaddition of the primary product ketone to benzene. Mixtures of benzene and $\alpha,\alpha,\alpha$-trifluoroacetophenone show a new absorption maximum at 268 nm in the presence and absence of trifluoroacetic acid or methanol which is attributed to a charge-transfer transition between benzene and the ketone. Excitation within this absorption band is suggested to form initially the spin-paired radical-ion pair **137** which becomes stabilised by radical combination to give zwitterion **138**, and protonation on oxygen (though not necessarily in this order). Deprotonation from carbon yields the alcohol **135**. It is relevant to note here that photoreduction of $\alpha,\alpha,\alpha$-trifluoroacetophenone by toluene to yield the pinacol **134** occurs in the absence of added acid, and the methyl group acts as the hydrogen donor: no reaction at the ring carbon atoms appears to occur in this case.[169] The weaker acceptor acetophenone does not show charge-transfer absorption with benzene, and does not photoadd.

The formation of trifluoroacetophenone from benzene and trifluoroacetic acid is an example of *photo-Friedel–Crafts acylation*, and is thus related to the acid-catalysed photoelectrophilic substitution reactions with maleic anhydride and dimethyl acetylenedicarboxylate mentioned in Sections 3.1.3 and 3.2.[81] Other related systems have been investigated: thus whereas acetyl chloride and benzene gave acetophenone, acetic anhydride was photochemically inert towards benzene.[168]

It will be noted that the zwitterionic intermediates (e.g. **43**, **136** and **138**) proposed for these photoelectrophilic substitutions are structurally related to the Wheland intermediates involved in more conventional thermal electrophilic substitutions.

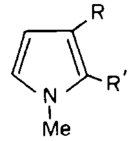
The photoethoxycarbonylmethylation of benzene with ethyl halogenoacetates has been studied in the presence of Lewis acids.[170] Only the "Friedel–Crafts" product **139** is formed; the absence of diethyl succinate tends to discount the involvement of ethoxycarbonylmethyl radicals in the mechanism. In the absence of Lewis acids, diethyl succinate and **139** are formed in approximately equal amounts[171] (see Ref. 172 for photo-Friedel–Crafts reactions of chloroacetamide with anisole and phenol).

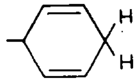
Light induced alkylation of benzene has also been noted in the formation of 1,1,2-triphenylethane from irradiation of 1,1-diphenylethylene in benzene, but no mechanistic details are yet available.[173]

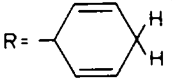
The reactions of benzene with photo-generated free radicals, carbenes, etc. are not reviewed here, nor are the reactions of aryl radicals generated photochemically, e.g. from diarylmercury compounds or aryl iodides: these are essentially thermal processes. However, one report which at first sight might appear to be a simple radical process is included as the mechanism has interesting features and there are no clear analogues in thermal chemistry. It was mentioned in Section 2 that hexafluorobenzene and benzene form a 1:1 molecular complex.[17] Although we were initially hopeful that irradiation of this might lead to "dimerisation" of the aromatic systems, the substitution product 2,3,4,5,6-pentafluorobiphenyl, and biphenyl and decafluorobiphenyl were formed in the molecular ratio 100:3:1.[18] The intermediacy of phenyl radicals was discounted by the observation that thermal and photochemical generation of such radicals in equimolar mixtures of the aromatic compounds led to some ten times more biphenyl than 2,3,4,5,6-pentafluorobiphenyl. The evidence concerning the possible involvement of pentafluorophenyl radicals is apparently conflicting. On the one hand it has been found that the thermal generation of these radicals in an equimolar mixture of the arenes produces pentafluoro- and decafluoro-biphenyl in the molecular ratio 100:0.7 which is in good agreement with that found from irradiation of benzene-hexafluorobenzene mixtures. Further, similar thermal generation of the pentafluorophenyl radicals in toluene gave *o*-, *m* and *p*-(pentafluorophenyl)toluenes in ratios which were in excellent agreement with those found from irradiation of an equimolecular mixture of toluene and hexafluorobenzene. Although these findings seemingly provide very strong evidence for the involvement of pentafluorophenyl radicals, it is difficult on the other hand to reconcile them with the following factors. Firstly the dissociation energy of the aromatic C–F bond (520 kJ mol$^{-1}$ in $C_6F_6$) is considerably higher than the quantal energy of the exciting radiation (254 nm, 468 kJ mol$^{-1}$). Furthermore, the reaction is also very solvent dependent, and tract amounts (0.085 M) of acetonitrole, methanol and trifluoroacetic acid increase the rate of reaction under standard conditions by factors of 30, 100 and 400% respectively. This strong dependence of an apparently homolytic process on the presence of polar molecules and proton donors is highly unusual. A further curious feature of this reaction is that naphthalene has been found to photosensitise the formation of 2,3,4,5,6-pentafluorobiphenyl, and this process is also promoted by polar solvents. The only exothermic energy transfer process is also promoted by polar solvents. The only exothermic energy transfer process available in this system would involve $S_1$ naphthalene and either $T_1$ benzene or $T_1$ hexafluorobenzene. The naphthalene sensitisation therefore suggests a novel phenomenon whereby complexing of $S_1$ naphthalene in an exciplex with, say, $S_0$ hexafluorobenzene promotes intersystem

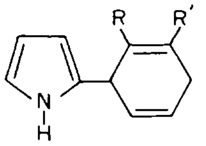
---

† As we have previously noted, the irradiation of benzene in the presence of weaker acids such as acetic acid, or acidified alcohols or water, leads to the formation of substituted bicyclo [3,1,0]hex-2-enes by acidolysis of benzvalene.[1,21]

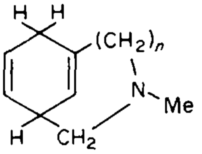


(125) R = H, R' = 

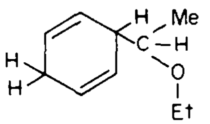
(126) R =  , R' = H



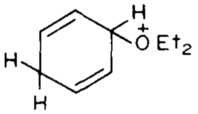
(127) R = H, R' = Me
(128) R = Me, R' = H



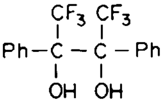
(129) n = 3
(130) n = 4



(131)

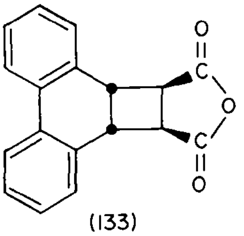


(132)

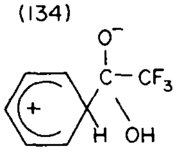


$Ph-C(CF_3)(OH)-C(CF_3)(OH)-Ph$

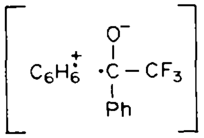
(134)



(133)

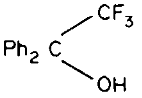


(136)



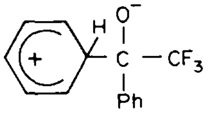
$[C_6H_6^{+\bullet}\ \bullet C(O^-)(CF_3)Ph]$

(137)



$Ph_2C(CF_3)OH$

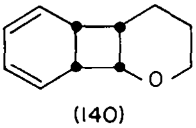
(135)



(138)

$PhCH_2CO_2Et$

(139)



(140)

crossing and dissociation to produce the triplet hexafluorobenzene plus $S_0$ naphthalene, a process possibly aided to some extent by spin-orbit perturbation induced by the combined effect of six fluorine atoms. We note here a close analogy with the benzene excimer which dissociates to $T_1$ benzene.[13] The unsensitised reaction is promoted in the presence of heavy-atom solvents, and is quenched by oxygen, consistent with a triplet intermediate. In contrast, the naphthalene-sensitised process is strongly inhibited in the presence of heavy-atom solvents, doubtless by competitive promotion of the formation of triplet naphthalene.[18]

All in all, therefore, the evidence relating to this strange reaction appears to indicate the necessary involvement of $T_1$ hexafluorobenzene and the formation of this via one or more exciplexes having marked dipolar character. In the absence of any obvious route from $T_1$ hexafluorobenzene to the pentafluorophenyl radical, it seems necessary to postulate that these two species may have closely similar patterns of reactivity in homolytic aromatic substitution processes. The intermediacy of pentafluorophenyl radicals in the photoreaction of hexafluorobenzene with benzene must apparently be discounted, despite the strong experimental evidence in favour of these. The key step is evidently a reaction of $T_1$ hexafluorobenzene with $S_0$ benzene in which $T_1$ hexafluorobenzene mimics the reactivity characteristics of the pentafluorophenyl radical.[18]

Photosubstitution reaction reactions which yield aniline derivatives from the irradiation of aliphatic amines and benzene have been mentioned in Section 3.4.

## 5. PRACTICAL ASPECTS

The practical synthetic organic chemist who is not particularly interested in photochemistry as such will no doubt wish to know what quantities of products can be conveniently obtained from these diverse reactions. The chemical yields of photoproducts are determined by several main factors, namely (a) quantum yields, (b) the photostability of the product (and related to this, the emission characteristics and wattage of the lamp), (c) the transmission of the cell material (normally silica, or borosilicate glass for wavelengths > 290 nm), (d) any tendency for the transmitting surfaces to become occluded by solid reaction products or resinous material, and (e) any tendency to form coloured reaction by-products which complete for the available radiation (e.g. in the addition of amines to benzene, the rigorous exclusion of oxygen is necessary to prevent the formation of brown photo-oxidation products of the amines).

Most of the major addition reactions we have described here have quantum yields within the range 0.05–0.5. Bearing in mind the above factors which can affect the chemical yield, this means that in practice gram quantities of the various adducts can usually be obtained using conventional commercial photochemical apparatus such as the Hanovia 1-litre reactor. In some cases, and particularly when medium- rather than low-pressure mercury lamps are used, resinous deposits tend to form on the cell surface, and can render this almost opaque to ultraviolet radiation. A special constant-transmission "scraper cell" (Fig. 9) has been designed to overcome the difficulty.[174]† The use of this can increase dramatically (e.g. × 30) the chemical yields of some products, particularly cyclo-octatetraenes from acetylenes and benzene, and the photoadducts of amines with benzene. A conventional cell is satisfactory for many photoreactions, and for quantum yield determinations over short irradiation times, but use of the "scraper cell" for preparative applications is never disadvantageous, and sometimes virtually essential.

Some idea of the preparative utility of these reactions may be gained from the following examples.

The 2:1 photoaddition of maleic anhydride to benzene to yield **38a** proceeds very effectively in sunlight in Pyrex flasks, especially when photosensitised by benzophenone,[175] and has been adapted as a student preparation.[176] The insoluble adduct crystallises from solution. The sunlight procedure could be used for production of this compound and related adducts on a kilogram scale with very simple apparatus.

Formation of the 1,3-photoadduct (type **15**) of benzene and *cis*-cyclo-octene can be conveniently accomplished in a Hanovia 1-litre photochemical reactor using a 100-W medium pressure mercury lamp. Irradiation of a 1:1 mixture of the reactants can give some 30 g of crude product in a 20 hr period. The highest quantum yield ($\Phi = ca.\ 0.7$) for a benzene addition reaction which we have yet observed is for the reaction with dihydropyran to give the 1,2-cycloadduct **140**.[63] The irradiation of 1.0 M benzene and 3.5 M dihydropyran solutions in iso-octane with a 15-W low-pressure lamp yields a 0.02-M solution of the adduct in approximately 45 min.

The synthesis of cyclo-octatetraenes by photoaddition of acetylenes to benzene has proved of practical value in a number of applications (Ref. 106). With unconjugated and unstrained acetylenes the low quantum yields necessitate prolonged periods of irradiation,[34] but in other cases the additions occur more readily. Thus irradiation of dimethyl acetylenedicarboxylate (4 ml) in benzene (150 ml) for 20 hr at 50–55° using a 500-W medium pressure mercury lamp and a "scraper cell" gave dimethyl cyclo-octatetraene-1,2-dicarboxylate (2 g).[105]

## 6. CONCLUSION

When one considers that virtually all knowledge of the organic photochemistry of the benzene ring has been obtained within the past 20 years, the extensive range of isomerisation, addition, and substitution reactions surveyed in this two-part review appears especially remarkable. Most of the reactions are without parallel in thermal chemistry, and many provide compounds at present difficult or impossible of access by non-photochemical routes. It is already clear that the photochemistry of benzene, most of it involving the $S_1$ state, is considerably more varied than the classical thermal chemistry, and in many ways more appropriate to the hypothetical cyclohexatriene than that highly resonance-stabilised hexagonal molecule of which generations of chemists have read in their textbooks. (We emphasise that this remark applies only as a guide to the chemical

---

†A complete "scraper cell" unit is available commercially from Hanovia (the "*Reading Reactor*" Ref. no. 17614/1).

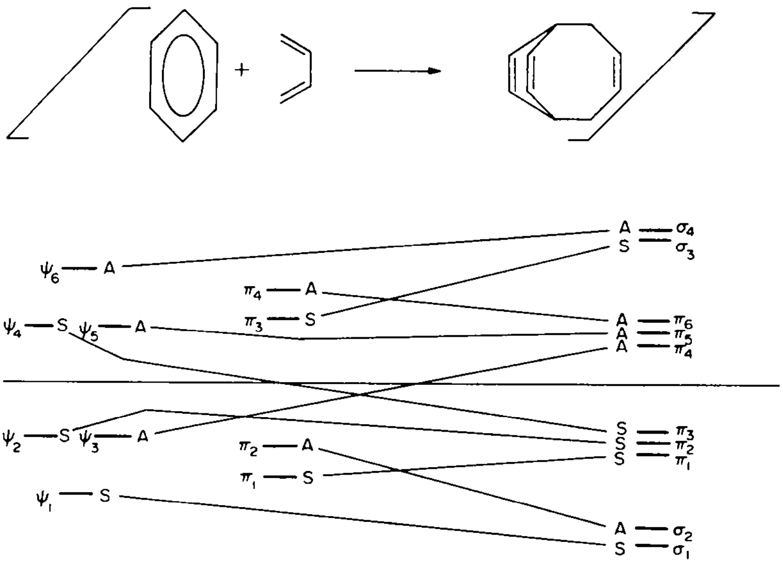


Fig. 5. *para*/*cis*-1,4-Addition of *cisoid*-buta-1,3-diene to benzene.

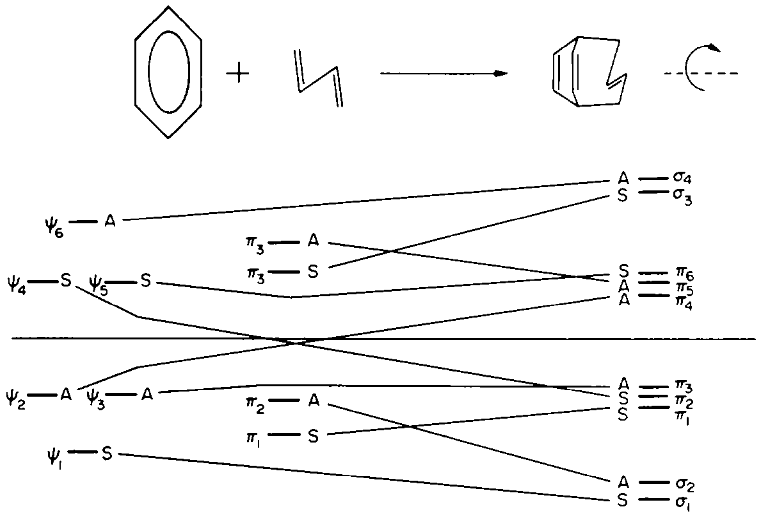


Fig. 6. *para*/*trans*-1,4-Addition of *transoid*-buta-1,3-diene to benzene.

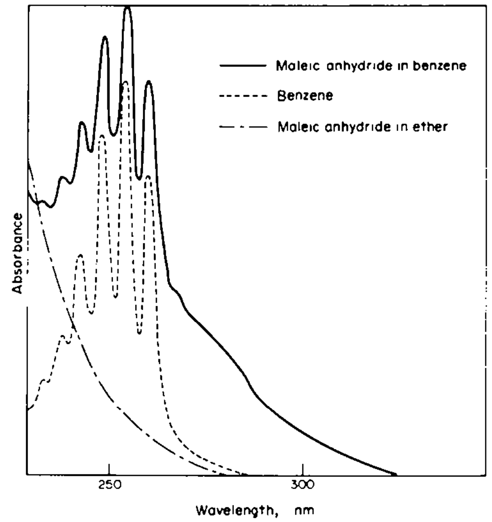


Fig. 7. UV spectra of maleic analydride in benzene and ether.[92]

properties: $S_1$ benzene does not have the bond-alternation expected for cyclohexatriene). It is perhaps in the isomerisations to fulvenes, benzvalenes, Dewar-benzenes, etc. that the photoexcited benzene ring appears at its most protean; but the strong tendency for photoaddition to other molecules provides a useful and interesting complement to the substitution reactions so characteristic of the thermal chemistry.

In general, orbital symmetry analyses have proved of considerable value in unravelling the mechanistic complexities presented by a sometimes bewildering choice of reaction pathways. Even in cases such as the 1,2-cycloaddition of certain alkenes which the reaction is stereospecific but formally symmetry-forbidden as a concerted process, the orbital symmetry analyses provided an important clue to the polar factors which had not previously been suspected to be important in such reactions. Anthough the main mechanistic patterns are beginning to emerge, much detailed photophysical work remains to be done, particularly in connection with the nature and role of intermediate complexes. Likewise,

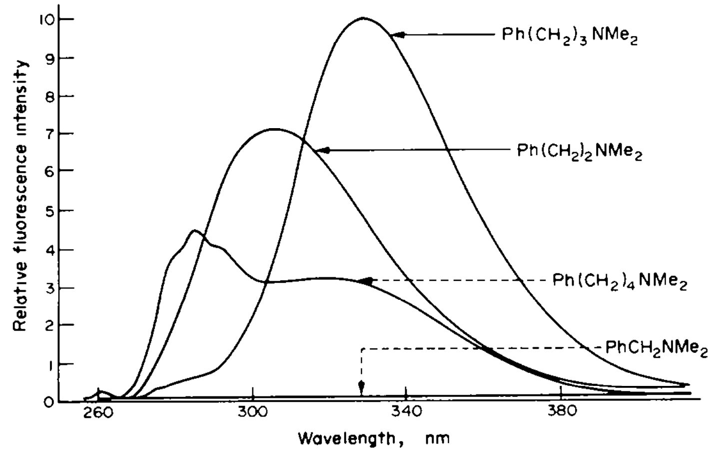


Fig. 8. Fluorescence spectra of $Ph(CH_2)_nNMe_2$: excitation wavelength 260 nm.

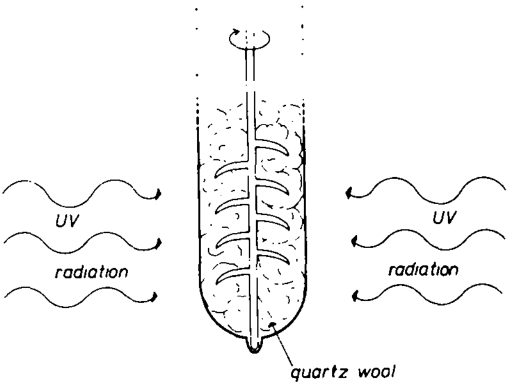


Fig. 9. Principle of the "Scraper-cell" (Ref. 174).

many gaps and shadowy areas remain in the organic photochemistry, e.g. substituent effects.

Thus the photochemistry of the benzene ring is a broad but only recently explored area of chemistry which while posing major problems in theoretical and physical photochemistry is also providing many new opportunities in organic synthesis. And it is an area which can yield great enjoyment to the researcher, as we are pleased to testify.

## APPENDIX

Added in Proof (August 1977).

Since submission of the manuscript in July 1976, the following significant reports have appeared.

Concerning the 1,3-cycloaddition of ethylenic compounds to the benzene ring which is normally insensitive to solvent polarity, Gilbert and Taylor have observed that ethyl vinyl ether readily undergoes 2,6-cycloaddition to anisole in a process which is markedly promoted by the use of polar solvents.[177] Mirbach *et al.* have reported that propene (I.P. 9.73 eV) undergoes exclusive 1,3-photoaddition to benzene, and ethylene (I.P. 10.5 eV) 1,3-photoaddition together with a comparable degree of 1,2-photoaddition.[178] Application of the empirical relationship suggested in Ref. 16 would have led one to expect predominant 1,2-addition of both alkenes, although the higher degree of 1,2-addition for ethylene is in accord with the proposed dependence on ionisation potential differences. The authors have reasonably suggested that for alkenes which act as acceptors relative to benzene, electron affinities may provide a better index than ionisation potentials for predicting the relative competing tendencies for 1,2- and 1,3-photoaddition.

Scharf and Mattay have reported that 2,2-dimethyl-1,3-dioxole (I.P. 7.92 eV) undergoes predominant 1,2-photoaddition to benzene, in accord with the empirical rule in Ref. 16, but that the adduct has *exo* stereochemistry in contrast with the *endo* stereochemistry observed previously for donor ethylenes.[179] NMR studies have however indicated that the precursor "dark" complex between the dioxole and benzene is also unusual in being of *exo* type.[180]

Sket and Zupan have described some examples of the photoaddition of ethylenes to hexafluorobenzene which, unlike the additions reported in Refs. 60, 71 and 72, lead exclusively to adducts of 1,2-type: 1,4-dihydronaphthalene gave exclusively an *endo*-adduct, whereas cyclopentene gave mainly the *exo*-adduct with a minor proportion of the *endo* isomer.[181] The major primary photoproduct from norbornadiene and hexafluorobenzene appears to be a very labile *exo-syn* 1,2-adduct.[182] It would seem likely that these differences reflect differences in the stereochemistry of precursor "dark" complexes, although there is as yet no experimental information on this point. 1,2-Photoadducts rather than cyclooctatetraenes have been obtained from certain acetylenes and hexafluorobenzene.[183]

Russian workers[184] have proposed a revised structure for a previously described[185] photoproduct from dichloromaleic anhydride and benzene. The photoreaction of fumarodinitrile with benzene has been reported to give phenylsuccinodinitrile as a major product.[186]

## REFERENCES

[1] Part I: D. Bryce-Smith and A. Gilbert, *Tetrahedron* **32**, 1309 (1976).

[2] E. Havinga and J. Cornelisse, *Chem. Rev.* **75**, 353 (1975); J. Cornelisse, *Pure Appl. Chem.* **41**, 433 (1975); E. Havinga and J. Cornelisse, *Ibid.* **47**, 1 (1976); J. den Heijer, O. B. Shadid, J. Cornelisse and E. Havinga, *Tetrahedron* **33**, 779 (1977).

[3] *Photochemistry of Aromatic compounds*, A. Gilbert in *Photochemistry*, (Edited by D. Bryce-Smith) Specialist Periodical Reports, Volumes 1–8 inclusive. The Chemical Society, London, (1970–1977).

[4] J. Fritzsche, *J. Prakt. Chem.* **101**, 337 (1866).

[5] For a review of photodimerisation of anthracenes see D. O. Cowan and R. Drisko, *Elements of Organic Photochemistry*, Chap. 2, Plenum Press, New York (1975).

[6] H. Bouas-Laurent, R. Lapouyade, A. Castellan, A. Nourmamode and E. A. Chandross, *Z. Phys. Chem.* **101**, 39 (1976).

[7] B. K. Selinger and M. Sterns, *Chem. Comm.* 978 (1969); C. Kowala, G. Sugowdz, W. H. F. Sasse and J. A. Wunderlich, *Tetrahedron Letters* 4721 (1972); T. Teitei, D. Wells and W. H. F. Sasse, *Ibid.* 367 (1974).

[8] T. W. Mattingly, J. E. Lancaster and A. Zweig, *Chem. Comm.* 595 (1971).

[9] See for example N. Boens, M. de Brackelaire, J. Huybrechts and F. C. de Schryver, *Z. Phys. Chem.* **101**, 417 (1976); R. S. Davidson and T. D. Whelan, *Chem. Comm.* 361 (1977).

[10] N. L. Goldman and R. A. Ruden, *Tetrahedron Letters* 3951 (1968).

[12] N. Dennis, A. R. Katritzky and H. Wilde, *J. Chem. Soc. Perkin I*, 2338 (1976).

[13] R. B. Cundall and D. A. Robinson, *J. Chem. Soc.* Faraday II **68**, 1691 (1972).

[14] G. Schröder, W. Martin and H. Röttele, *Angew. Chemie.* Internat. Edn. **8**, 69 (1969).

[15] D. Bryce-Smith, *Chem. Comm.* 806 (1969).

[16] D. Bryce-Smith, A. Gilbert, B. H. Orger and H. M. Tyrrell, *Ibid.* 334 (1974).

[17] C. R. Patrick and G. S. Prosser, *Nature* **187**, 1021 (1960); J. C. A. Boeyens and F. H. Herbstein, *J. Phys. Chem.* **69**, 2153 (1965).

[18] D. Bryce-Smith, A. Gilbert and P. J. Twichett, *Chem. Comm.* 457 (1973).

[19] N. J. Turro and P. Lechtken, *J. Am. Chem. Soc.* **94**, 2886 (1972).

[20] R. Walsh, Private communication.

[21] K. E. Wilzbach, J. S. Ritscher and L. Kaplan, *J. Am. Chem. Soc.* **88**, 2881 (1966); J. A. Berson and N. M. Hasty, *Ibid.* **93**, 1549 (1971); T. J. Katz, E. J. Wang and N. Acton, *Ibid.* **93**, 3782 (1971); L. Kaplan, D. J. Rausch and K. E. Wilzbach, *Ibid.* **94**, 8638 (1972); E. Farenhorst and A. F. Bickel, *Tetrahedron Letters* 5911 (1966).

[22] L. Kaplan, L. A. Wendling and K. E. Wilzbach, *J. Am. Chem. Soc.* **93**, 3821 (1971).

[23] M. Luria and G. Stein, *J. Phys. Chem.* **76**, 165 (1972).

[24] See also J. Irina and K. C. Kurien, *Chem. & Ind.* 763 (1972); J. Irina and K. C. Kurien, *Chem. Comm.* 738 (1973) and Y. Ilan, M. Luria and G. Stein, *J. Phys. Chem.* **80**, 584 (1976).

[25] B. Stevens and B. E. Algar, *Ibid.* **72**, 3468 (1968).

[26] J. Rigaudy, *Pure Appl. Chem.* **16**, 169 (1968).

[27] C. S. Foote, S. Mazur, P. A. Burns and D. Lerdal, *J. Am. Chem. Soc.* **95**, 586 (1973).

[28] G. Rio and J. Berthelot, *Bull. Soc. Chim. Fr.* 822 (1971).

[29] A. Morikawa, S. Brownstein and R. J. Cvetanovic, *J. Am. Chem. Soc.* **92**, 1471 (1970).

[30] K. E. Wilzbach and L. Kaplan, *Ibid.* **93**, 2073 (1971).

[31] B. H. Orger, Ph.D. Thesis, Reading University (1969).

[32] D. Bryce-Smith, *Pure Appl. Chem.* **34**, 193 (1973).

Edn. **14**, 552 (1975).

[33] W. I. Feree, J. B. Frutzner and H. Morrison, *J. Am. Chem. Soc.* 43, 5502 (1971).

[34] D. Bryce-Smith, A. Gilbert and J. Grzonka, *Chem. Comm.* 498 (1970).

[35] R. C. Dougherty, *J. Am. Chem. Soc.* **93**, 7187 (1971).

[36] See, e.g. D. Bryce-Smith and A. Gilbert, *Chem. Comm.* 1701 (1968).

[37] K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.* **88**, 2066 (1966).

[38] D. Bryce-Smith, A. Gilbert and B. H. Orger, *Chem. Comm.* 512 (1966).

[39] See, e.g. Refs. 16 and 40.

[40] R. Srinivasan, *J. Phys. Chem.* **76**, 15 (1972).

[41] R. Srinivasan, *Tetrahedron Letters* 4551. (1971).

[42] W. R. Roth and B. Peltzer, *Liebigs Ann.* **685**, 56 (1965).

[43] R. Srinivasan, *I. B. M. J. Res. Develop* **15**, 34 (1971).

[44] J. Cornelisse and R. Srinivasan, *Chem. Phys. Letters* **20**, 278 (1973).

[45] R. Srinivasan, *J. Am. Chem. Soc.* **94**, 8117 (1972).

[46] R. Srinivasan, *Tetrahedron Letters* 2725 (1974).

[47] E. L. Allred and B. R. Beck, *J. Am. Chem. Soc.* **95**, 2393 (1973).

[48] A. Gilbert, Unpublished work.

[49] A. Gilbert and M. W. B. Samsudin, Unpublished work.

[50] V. Y. Merritt, J. Cornelisse and R. Srinivasan, *J. Am. Chem. Soc.* **95**, 8250 (1973).

[51] A. Gilbert and J. Forrester, Unpublished work.

[52] A. Gilbert and M. W. B. Samsudin, *Angew. Chem.* Internat. Edn. **14**, 552 (1975).

[53] H-G. Heine and W. Hartmann, *Ibid.* Internat. Edn. **14**, 698 (1975).

[54] D. Bryce-Smith and A. Gilbert, *Chem. Comm.* 643 (1966).

[55] J. Cornelisse, V. Y. Merritt and R. Srinivasan, *J. Am. Chem. Soc.* **95**, 6197 (1973).

[56] R. Srinivasan, *Ibid.* **93**, 3555 (1971).

[57] R. Srinivasan, V. Y. Merritt and G. Subrahmanyam, *Tetrahedron Letters* 2715 (1974); J. A. Ors and R. Srinivasan, *J. Org. Chem.* **42**, 1321 (1977).

[58] H. M. Tyrrell, Ph. D. Thesis, Reading University (1974).

[59] C. S. Angadiyavar, J. Cornelisse, V. Y. Merritt and R. Srinivasan, *Tetrahedron Letters* 4407 (1973).

[60] D. Bryce-Smith, B. E. Foulger, A. Gilbert and P. J. Twichett, *Chem. Comm.* 794 (1971).

[61] J. G. Atkinson, D. E. Ayer, G. Büchi and E. W. Robb, *J. Am. Chem. Soc.* **85**, 2257 (1963).

[62] T. S. Cantrell, *Ibid.* **94**, 5929 (1972); N. C. Yang, B. Kim, W. Chiang and T. Hamada, *Chem. Comm.* 729 (1976).

[63] A. Gilbert and G. Taylor, *Tetrahedron Letters* 469 (1977).

[64] B. E. Job and J. D. Littlehailes, *J. Chem. Soc.* (C) 886 (1968).

[65] H. D. Scharf and R. Klar, *Chem. Ber.* **105**, 575 (1972); H. D. Scharf, H. Leismann, W. Erb, H. W. Gaidetzka and J. Aretz, *Pure Appl. Chem.* **41**, 581 (1975).

[66] H. M. Tyrrell and A. P. Wolters, *Tetrahedron Letters* 4193 (1974).

[67] R. J. Atkins, G. I. Fray and A. Gilbert, *Ibid.* 3087 (1975).

[68] D. Bryce-Smith, G. I. Fray and B. Vickery, *J. Chem. Soc.* (C) 390 (1967).

[69] D. Bryce-Smith, A. Gilbert and H. M. Tyrrell, *J. Chem. Soc. Chem. Comm.* 699 (1974).

[70] R. M. Bowman, C. Calvo, J. J. McCullough, R. C. Miller and I. Singh, *Canad. J. Chem.* **51**, 1060 (1973).

[71] D. Bryce-Smith, A. Gilbert and B. H. Orger, *Chem. Comm.* 800 (1969).

[72] P. J. Twitchett, Ph.D. Thesis, Reading University (1972).

[73] D. Bryce-Smith, *Pure Appl. Chem.* **16**, 47 (1968).

[74a] H. J. F. Angus and D. Bryce-Smith, *Proc. Chem. Soc.* 326 (1959); *J. Chem. Soc.* 4791 (1960); [b] E. Grovenstein, D. V. Rao and J. W. Taylor, *J. Am. Chem. Soc.* **83**, 1705 (1961); [c] G. O. Schenck and R. Steinmetz, *Tetrahedron Letters* No. 21, 1 (1960); [d] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.* 2675 (1962); [e] G. S. Hammond and W. M. Hardham, *Proc. Chem. Soc.* 63 (1963); and *J. Am. Chem. Soc.* **89**, 3200 (1967); [f] J. S. Bradshaw, *J. Org. Chem.* **31**, 3974 (1966).

[75] D. Bryce-Smith and M. A. Hems, *Tetrahedron Letters* No. 17, 1895 (1966).

[76] J. S. Bradshaw, *Ibid.* No. 18, 2039 (1966).

[77] D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.* 918 (1965).

[78] D. Bryce-Smith, B. E. Connett and A. Gilbert, *Ibid.* (C) 816 (1968).

[79] C. E. Rees, Ph.D. Thesis, Reading University (1973).

[80] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.* **75**, 3776 (1953).

[81] D. Bryce-Smith, R. Deshpande, A. Gilbert and J. Grzonka, *Chem. Comm.* 561 (1970).

[82] D. Bryce-Smith and A. Gilbert, *Ibid.* 19 (1968).

[83] S. H. Shaikhrazieva, E. V. Talvinskii and G. A. Tolstikov, *Zh. Org. Khim.* **10**, 663 (1974).

[84] D. Bryce-Smith and M. A. Hems, *J. Chem. Soc.* (B) 812 (1968).

[85] G. A. Olah, *J. Am. Chem. Soc.* **87**, 1103 (1965).

[86] W. Hartmann, H. G. Heine and L. Schrader, *Tetrahedron Letters* 883 (1974).

[87] W. Hartmann, H. G. Heine and L. Schrader, *Ibid.* 3101 (1974).

[88] D. Bryce-Smith, R. Deshpande and A. Gilbert, *Ibid.* 1627 (1975).

[89] G. Koltzenburg, S. G. Fuss, S. P. Mansfield and G. O. Schenck, *Ibid.* 1861 (1966).

[90] G. Koltzenburg, K. Kraft and G. O. Schenck, *Ibid.* 353 (1965).

[91] G. Koltzenburg, Personal communication.

[92] R. R. Deshpande, Ph.D. Thesis, Reading University (1971).

[93] M. A. Hems, Ph.D. Thesis, Reading University (1967).

[94] D. Bryce-Smith, R. Deshpande, A. Gilbert and M. A. Hems, Unpublished work.

[95] D. Bryce-Smith, A. Gilbert and B. Halton, Unpublished work.

[96] D. Bryce-Smith, G. J. Bullen, N. H. Clark, B. E. Connett and A. Gilbert. *J. Chem. Soc.* (C) 167 (1966).

[97] A. S. Kushner, *Tetrahedron Letters* 3275 (1971).

[98] D. Bryce-Smith, B. E. Foulger and A. Gilbert, *J. Chem. Soc.* Chem. Comm., 664 (1972).

[99] N. C. Perrins and J. P. Simons, *Trans. Faraday Soc.* **65**, 390 (1969).

[100] D. Bryce-Smith, B. E. Foulger and A. Gilbert, *J. Chem. Soc.* Chem. Comm. 769 (1972).

[101] A. C. Gray, T. Kakihana, P. M. Collins and H. Hart, *J. Am. Chem. Soc.* **89**, 4556 (1967).

[102] S. Leach and E, Migirdicyan, *J. Chim. Phy.* 762 (1961).

[103] P. Lechtken and G. Hesse, *Liebigs Ann.* **754**, 8 (1971).

[104] E. Grovenstein and D. V. Rao, *Tetrahedron Letters* 148 (1961).

[105] D. Bryce-Smith and J. E. Lodge, *Proc. Chem. Soc.* 333; (1961) *J. Chem. Soc.* 695 (1963).

[106] L. A. Paquette, *Tetrahedron* **31**, 2855 (1975), lists further Refs. in a general review of cyclo-octatetraenes.

[107] D. Bryce-Smith, A. Gilbert and J. Grzonka, *Angew. Chem.* Internat. Edn. **10**, 746 (1971).

[108] R. D. Miller and V. Y. Abraitys, *Tetrahedron Letters* 891 (1971).

[109] W. Lippke, W. I. Feree and H. Morrison, *J. Am. Chem. Soc.* **96**, 2134 (1974).

[110] H. Morrison, T. Nylund and F. Palensky, *Chem. Comm.* 4 (1976).

[111] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.* 695 (1963).

[112] G. Buchi, C. W. Perry and E. W. Robb, *J. Org. Chem.* **27**, 4106 (1962).

[113] K. Ota, K. Murofushi, T. Hoshi and H. Inoue, *Tetrahedron Letters* 1431 (1974).

[114] R. S. H. Liu and C. G. Krespan, *J. Org. Chem.* **34**, 1271 (1969).

[115] See p. 500 in Vol. 2 of *Specialist Periodical Reports on Photochemistry*, The Chemical Society, London.

[116] T. Teitei and D. Wells, *Tetrahedron Letters* 2299 (1975).

[117] Y. Katsuhara, T. Nakamura, A. Shimizu, Y. Shigemitsu and Y. Odaira, *Chem. Letters* 1215 (1972).

[118] E. Grovenstein, T. C. Campbell and T. Shibata, *J. Org. Chem.* **34**, 2418 (1969).

[119] K. Kraft and G. Koltzenburg, *Tetrahedron Letters* 4357, 4723 (1967).

[120] K. Kraft, Ph.D. Thesis, University of Bonn (1968).

[121] H. P. Loeffler, *Tetrahedron Letters* 787 (1974).

[122] G. Kaupp, *Angew. Chem.* Internat. Edn. **84**, 718 (1972).

[123] N. C. Yang and J. Libman, *J. Am. Chem. Soc.* **94**, 1405 (1972).

[124] N. C. Yang, J. Libman, L. W. Barrett, M. H. Hui and R. L. Loeschen, *Ibid.* **94**, 1406 (1972).

[125] N. C. Yang, D. M. Shold and J. K. McVey, *J. Am. Chem. Soc.* **97**, 5004 (1975); N. C. Yang, K. Srinivasachar, B. Kim and J. Libman, *Ibid.* 5006.

[126] N. C. Yang, J. Libman and M. F. Savitzky, *Ibid.* **94**, 9226 (1972).

[127] J. Libman, *Chem. Comm.* 361 (1976).

[128] T. Sasaki, K. Kanematsu and J. Hayakawa, *J. Am. Chem. Soc.* **95**, 5632 (1973).

[129] N. C. Yang and K. Srinivasachar, *Chem. Comm.* 48 (1976).

[130] N. C. Yang and J. Libman, *Tetrahedron Letters* 1409 (1973).

[131] J. C. Berridge, D. Bryce-Smith and A. Gilbert, *Ibid.* 2325 (1975).

[132] J. C. Berridge, D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.* Chem. Comm., 964 (1974).

[133] T. S. Cantrell, *Tetrahedron Letters* 3959 (1974).

[134] N. C. Yang, C. V. Neywick and K. Srinivasachar, *Ibid.* 4311 (1975).

[135] J. C. Berridge, D. Bryce-Smith, A. Gilbert and T. S. Cantrell, *J. Chem. Soc.* Chem. Comm. 611 (1975).

[136] J. C. Berridge, Ph.D. Thesis, University of Reading (1975).

[137] M. Bellas, D. Bryce-Smith and A. Gilbert, *Chem. Comm.* 862 (1967).

[138] M. Bellas, D. Bryce-Smith and A. Gilbert, *Ibid.* 263 (1967).

[139] D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin and C. Manning, *J. Chem. Soc.* Chem. Comm. 916 (1971).

[140] J. A. Barltrop and R. J. Owers, *Chem. Comm.* 1462 (1970).

[141] R. S. Davidson, *Ibid.* 1450 (1969).

[142] J. A. Barltrop, *Pure Appl. Chem.* **33**, 179 (1973).

[143] N. C. Yang and J. Libman, *J. Am. Chem. Soc.* **95**, 5783 (1973); S. Vaidyanthan and V. Ramakrishnan, *Indian J. Chem.* **13**, 257, (1975) and Refs. therein; N. C. Yang, D. M. Shold and B. Kim, *J. Am. Chem. Soc.* **98**, 6587 (1976).

[144] A. Gilbert and S. Krestonosich, unpublished observations.

[145] C. Manning, Ph.D. Thesis, University of Reading (1974).

[146] D. Bryce-Smith, A. Gilbert and C. Manning, *Angew. Chemie* Internat. Edn. **86**, 350 (1974).

[147] A. Weller, *Pure Appl. Chem.* **16**, 115 (1968).

[148] C. Pac and H. Sakurai, *Tetrahedron Letters* 3829 (1969).

[149] J. J. McCullough, W. S. Wu and C. W. Huang, *J. Chem. Soc.* Perkin II, 370 (1972).

[150] M. Ottolenghi, *Acc. Chem. Res.* **6**, 153 (1973) and Refs. therein.

[151] H. Knibbe, K. Röllig, F. P. Schäfer and A. Weller, *J. Chem. Phys.* **47**, 1184 (1967); N. Mataga, T. Okada and N. Yamamoto, *Chem. Phys. Letters* **1**, 119 (1967); K. Kaneta and M. Koizumi, *Bull. Chem. Soc. Japan* **40**, 2254 (1967); D. Rehm and A. Weller, *Ber. Bunsenges Phys. Chem.* **73**, 834 (1969); S. Murata, H. Kokubun and M. Koizumi, *Z. Phys. Chem. Frankfurt* **70**, 47 (1970).

[152] H. Leonhardt and A. Weller, *Ber. Bunsenges Phys. Chem.* **67**, 791 (1963); H. Knibbe, D. Rehm and A. Weller, *Ibid.* **72**, 257 (1968).

[153] M. Koizumi and Y. Yamashita, *Z. Phys. Chem. Frankfurt* **57**, 103 (1968); K. Kawai, N. Yamamoto and H. Tsubomura, *Bull. Chem. Soc. Japan* **42**, 369 (1969).

[154] D. Bryce-Smith, A. Gilbert and S. Krestonosich, *J. Chem. Soc. Chem. Comm.* 405 (1976).

[155] M. Bellas, D. Bryce-Smith, M. T. Clarke A. Gilbert, G. Klunklin, C. Manning, S. Krestonosich and S. Wilson, *J. Chem. Soc. Perkin I*, in the press.

[156] A. Gilbert and E. Stokes, unpublished observations.

[157] D. Bryce-Smith, A. Gilbert and G. Klunklin, *J. Chem. So* Chem. Comm. 330 (1973).

[158] See E. A. Chandross and H. T. Thomas, *Chem. Phys. Letters* **9**, 393 (1971), and D. R. G. Brimage and R. S. Davidson, *Chem. Comm.* 1385 (1971) for emission from naphthyl and anthryl alkylamines.

[159] D. Bryce-Smith and G. B. Cox, *Chem. Comm.* 915 (1971).

[160a] M. Ohashi and K. Tsujimoto, *Chem. Letters* **8**, 829 (1975).

[160b] K. Al-Fakhri and A. C. Pratt, *Chem. Comm.* 484 (1976).

[161] V. I. Stenberg and R. J. Perkins, *J. Org. Chem.* **27**, 4111 (1962); G. O. Schenck, J. Kuhls, S. P. Mannsfeld and C. H. Krauch, *Chem. Ber.* **96**, 813 (1963).

[162] D. Bryce-Smith and B. Vickery, *Chem. & Ind.* 429 (1961).

[163] R. A. Caldwell, *J. Am. Chem. Soc.* **95**, 1690 (1973).

[164] J. P. Simons, *Trans. Faraday Soc.* **56**, 391 (1960).

[165] R. Helder and H. Wynberg, *Tetrahedron Letters* 605 (1972); H. J. Kuhn and K. Gollnick, *Ibid.* 1909 (1972) and *Chem. Ber.* **106**, 674 (1973).

[166] C. Rivas, C. Perez and T. Nakano, *Rev. Latinoam. Quim.* **6**, 166 (1975).

[167] A. Lablache-Combier, *Éléments de Photochimie Avancée* (Edited by P. Courtot). Hermann, Paris (1972).

[168] D. Bryce-Smith, G. B. Cox and A. Gilbert, *J. Chem. Soc.* Chem. Comm. 914 (1971).

[169] P. J. Wagner and R. A. Leavitt, *J. Am. Chem. Soc.* **92**, 5806 (1970).

[170] Y. Izawa, T. Ishihara and Y. Ogata, *Tetrahedron* **28**, 211 (1972); Y. Ogata and E. Hayashi, *Bull. Chem. Soc. Jap.* **50**, 323 (1977).

[171] Y. Ogata, T. Itoh and Y. Izawa, *Bull. Chem. Soc., Japan* **42**, 794 (1969).

[172] O. Yonemitsu and S. Naruto, *Chem. and Pharm. Bull. Japan* **19**, 1158 (1971).

[173] M. Kawanisi and K. Matsunaga, *J. Chem. Soc.* Chem. Comm. 418 (1972).

[174] D. Bryce-Smith, J. A. Frost and A. Gilbert, *Nature* **213**, 1121 (1967).

[175] D. Bryce-Smith, A. Gilbert and B. Vickery, *Chem. & Ind.* 2060 (1962).

[176] R. E. Bozak and V. E. Alvarez, *J. Chem. Educ.* **47**, 589 (1970).

[177] A. Gilbert and G. Taylor, *Chem. Comm.* 242 (1977).

[178] M. F. Mirbach, M. J. Mirbach and A. Saus, *Tetrahedron Letters* 959 (1977).

[179] H. D. Scharf and J. Mattay, *Ibid.* 401 (1977).

[180] H. D. Scharf, private communication.

[181] B. Sket and M. Zupan, *Chem. Comm.* 1053 (1976) and 365 (1977).

[182] B. Sket and M. Zupan, *Tetrahedron Letters* 2811 (1977).

[183] B. Sket and M. Zupan, *J. Am. Chem. Soc.* **99**, 3504 (1977).

[184] V. S. Shaikhrazieva, E. V. Talvinskii and G. A. Tolstikov, *Izv. Akad. Nauk. SSSR Ser. Khim.* **7**, 1618 (1976).

[185] G. B. Vermont, P. X. Riccobono and J. Blake, *J. Am. Chem. Soc.* **87**, 4024 (1965).

[186] P. Schuler and H. Heusinger, *Photochem and Photobiol* **24**, 307 (1976).