# PHOTOADDITION AND PHOTOISOMERIZATION REACTIONS OF THE BENZENE RING

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## INTRODUCTION

The thermal chemistry of benzene and its derivatives has been extensively studied for well over a century, and constitutes one of the best-trodden fields of organic chemistry: its characteristic feature is the strong tendency for substitution reactions leading to products in which the aromatic ring survives. In marked contrast, the photochemistry of the benzene ring had been scarcely investigated at all prior to the present decade. About twenty different types of photochemical reactions involving the benzene ring have now become known, and nearly all of these lead to non-aromatic products. Herein lies a major difference between the thermal- and photo-chemistry of the benzene ring, a difference which provides a powerful stimulus for research into the nature of the photochemical processes involved, and an opportunity for the synthesis of molecules not readily accessible through thermal chemistry. Indeed, some of these molecules have quite exotic architecture. Our own interest in this field stems from the observation that liquid benzene can undergo photoisomerization to fulvene *via* the first optical transition[1].

The purpose of this lecture is to summarize both some new and previously known results on the photochemistry of benzene and its simple derivatives, and to present some mechanistic proposals which appear to collate much of the present information and may serve as a basis for future discussions and predictions.

## RESONANCE STABILIZATION IN THE BENZENE RING

The special chemical properties of the benzene ring loosely associated with its 'aromatic character' in ground-state chemistry are normally attributed to resonance stabilization. The resonance energy of benzene is often taken to be about 36 kcal mole$^{-1}$, although the proportion of this attributable to $\pi$-electron delocalization is rather uncertain. The quantal energy for ultra-violet radiation adsorbed by benzene in its $S_0 \rightarrow S_1$ transition is $c.$ 110 kcal mole$^{-1}$. This comparison shows that, quite apart from electronic considerations, the stabilization energy barrier to the formation of non-aromatic products is relatively unimportant in photochemistry; and benzene in its photochemical reactions does in fact often show behaviour which would be more appropriate to the hypothetical cyclohexatriene. (The comparison is potentially misleading, for the $S_0 \rightarrow S_1$ transition does not directly involve the lowest energy $\pi$-orbital, and $S_1$ benzene, of state $^1B_{2u}$, is an exactly planar regular hexagon in its equilibrium conformation[2]; but $T_0$

benzene, of state $^3B_{1u}$, has a deformed equilibrium conformation[3] suggestive of a degree of bond-alternation.)

Historically, the first photochemical reaction of an aromatic ring was provided one hundred years ago by Fritzsche in the production of photodimer (I) of anthracene[4]. A single example of this reaction in the naphthalene series is known[5]. Transannular additions of oxygen to anthracene and higher polycyclic aromatic hydrocarbons to give e.g.photo-oxide (II) have been reported



(I)          (II)

(III)
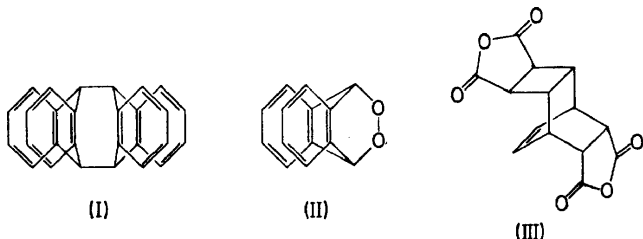
by Clar and Dufraisse and their collaborators[6]. The reactions involve singlet molecular oxygen, and have recently been shown to occur when this reagent is generated non-photochemically[7].

The 9,10-thermal photoaddition of maleic anhydride to anthracene is accelerated by ultraviolet irradiation[7a]. However, the photoaddition of maleic anhydride to benzene has no close parallel in thermal chemistry[8]. The product is the very stable 2:1-adduct (III) formed in a formal sense by *exo*-1,2- and *endo*-1,4-additions[9]. Reactions of this type can be photosensitized by benzophenone[10], and have been shown to involve charge-transfer excitation within a weak complex formed between the reactants[11]. Relatively electrophilic benzene derivatives such as benzonitrile and nitrobenzene show no such excitation with maleic anhydride and do not photoadd this reagent (although benzonitrile undergoes photoaddition of some simple olefins[12]); but the formation of a complex showing charge-transfer absorption is not in itself sufficient for photoaddition to be possible. Although increasing methylation of the benzene ring is well known to increase its donor character, methylation (and apparently substitution in general) markedly decreases the rate of photoaddition of maleic anhydride. Durene and hexamethylbenzene have not as yet been found to form adducts of the type (III) with maleic anhydride, although their mixtures with it show charge-transfer ultraviolet absorption†. Spectroscopic studies have shown that although the transition energy decreases with increasing methylation of the ring, the intensity of the absorption, measured under comparable conditions, *decreases* in the same order apart from the case of benzene itself. *Figures 1* and *2* show charge-transfer absorption spectra for solutions of maleic anhydride in some aromatic hydrocarbons measured with the use of 0·0002 cm cells. Durene and hexamethylbenzene, which are solids, were studied in chloroform solutions, so the corresponding values of $\epsilon_{apparent}$ are not strictly comparable‡. (The double

† Mesitylene has recently been found to undergo benzophenone-photosensitized addition of maleic anhydride to give the trimethyl derivative of adduct (III). The rate is much slower than that of the corresponding addition to *p*-xylene.

‡ $\epsilon_{apparent}$ is the extinction coefficient for a complex measured on the assumption that one of its component species (the acceptor in this case) is present wholly in the complexed form in the solution under examination.

maxima in many of the spectra will be discussed elsewhere.) With tetracyanoethylene and $p$-chloranil as acceptors in place of maleic anhydride, the intensity of charge-transfer absorption is virtually constant with increasing methylation of the aromatic ring if no third component such as
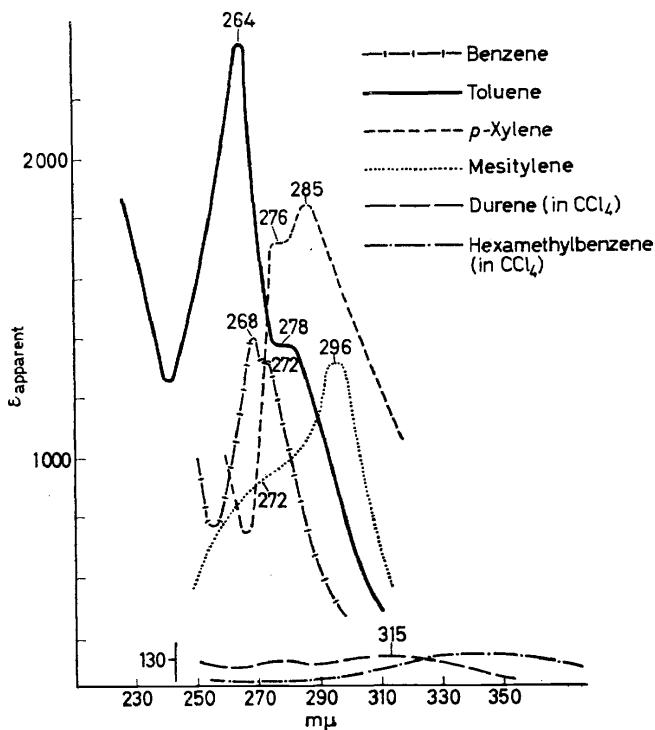


*Figure 1.* Charge-transfer absorption spectra for complexes of maleic anhydride and methylbenzenes

chloroform is used as solvent, and $\epsilon_{apparent} = \epsilon_{complex}$; but if an excess of chloroform is present, the absorption intensity increases with increasing methylation of the ring under comparable conditions (see *Table 1*).

These results suggest that the strong acceptors tetracyanoethylene and $p$-chloranil are essentially completely complexed in solutions of aromatic hydrocarbon donors; but they are incompletely complexed if these solutions are diluted with chloroform, the effective concentration of the complexed species being then dependent on the donor strength of the hydrocarbon. Maleic anhydride, in contrast, is a weaker acceptor and incompletely complexed in many pure aromatic hydrocarbon donors, as shown by the low values of $\epsilon_{apparent}$ (values above *c.* 1500 indicate that complexed maleic anhydride predominates). The degree of intermolecular interaction is in this case governed not only by the donor strength but also by steric effects: the second factor appears able to outweigh the first. Thus the fact that benzene undergoes photoaddition of maleic anhydride more readily than do

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toluene and higher methylbenzenes can be attributed to a favourable combination of accessibility and donor character which leads to the greatest interpenetration of donor and acceptor $\pi$-orbitals in the ground and excited states of a complex. These indications that the photoaddition of maleic
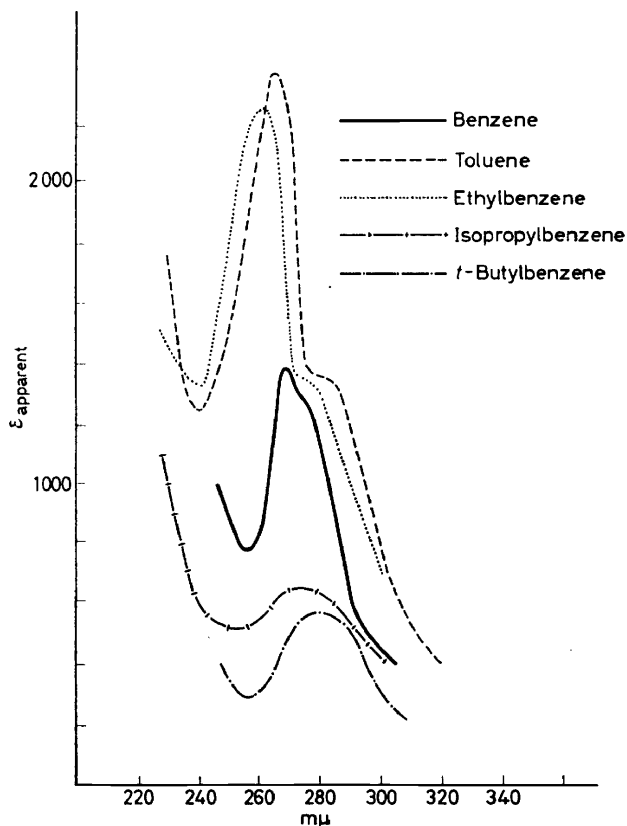


*Figure 2.* Charge-transfer absorption for complexes of maleic anhydride with monoalkyl-benzenes: no added solvent

*Table 1.* Ultraviolet spectroscopic data for charge-transfer transitions between aromatic donors and tetracyanoethylene

| Aromatic compound (ArH) | CHCl₃ *diluent* | | Excess of ArH *as solvent* | | Published values |
|---|---|---|---|---|---|
| | $\lambda_{max.}$ | $\epsilon_{apparent}$ | $\lambda_{max.}$ | $\epsilon_{apparent}$ | $\epsilon_{complex}$ |
| Benzene | 398 | 52·5 | 386 | 2580 | 2220, 3570 |
| Toluene | 419 | 65·0 | 410 | 2525 | 2500, 3330 |
| o-Xylene | 428 (460s) | 53 (48) | 431 | 2870 | 3330, 3860 |
| p-Xylene | 425 (470) | 115 (108) | 408 (453) | 1374 (1348) | 2650 |
| m-Xylene | 425 (450s) | 60 (45) | 436 | 3060 | 3300 |
| Mesitylene | 472 | 253 | 461 | 2970 | 2900, 3120 |
| Durene | 488 | 435 | | | |
| Hexamethylbenzene | 544 | 1100 | | | |
| t-Butylbenzene | 424 | 65 | | | |
| Di-t-butylbenzene | 425 | 26 | | | |

anhydride to benzene rings has a large steric requirement appeared at first to be supported by experimental evidence that the 1,2-cycloaddition step, believed to be largely rate-determining, occurred with high specificity at the ring positions most remote from existing substituents, viz. 3,4- in $C_6H_5R$ and 2,3- in $p$-$C_6H_4R_2$[13]. Recent work (with Dr. A. Gilbert) has shown that two isomeric 2:1 adducts are formed by benzophenone-sensitized photoaddition of maleic anhydride to toluene, $o$-, and $p$-xylene[13d]. In the case of $p$-xylene, infrared, ultraviolet, and n.m.r. spectroscopic data are consistent with provisional formulation of these adducts as the dianhydrides (IV) and (V).



(IV)            (V)
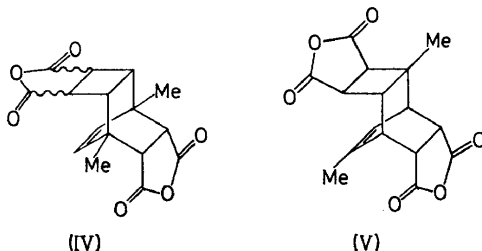
Adduct (IV) is that previously reported[13], but as yet we have reservations concerning the stereochemistry of the 2,3-addition step. Adduct (V) has not hitherto been described. It is a dimethyl derivative of the benzene–maleic anhydride adduct (III), but an *exo* 1,2-addition is involved in its formation rather than the *exo* 2,3-addition which would be expected on purely steric grounds. The pairs of isomeric adducts formed by $o$-xylene and toluene are structurally analogous to adduct (V)[13d].

Addition of maleic anhydride to $p$-xylene provides a rare example of a markedly temperature-dependent photochemical reaction. At 20°, adduct (IV) is formed almost exclusively, whereas at 110° adduct (V) is the major product. Intermediate mixtures are formed at intermediate temperatures. This kind of temperature effect has no close parallels, and is not at present well understood; but in view of the rôle played by donor–acceptor complexes in these addition processes it is tempting to ascribe it to a temperature dependence of the preferred conformation within a maleic anhydride–$p$-xylene complex in the electronic ground and/or excited states. Since the bonding energy within ground state complexes is so small, probably $< 5$ kcal, weak second order intermolecular effects may well assume a marked influence in determining the preferred orientation. The intensity of charge-transfer absorption in a $p$-xylene solution of maleic anhydride decreases smoothly as a function of temperature between 20° and 110°, but this effect could as well reflect a change in position in a single complex equilibrium as a change in preferred orientation. The question is being further studied.

It was suggested some years ago that the donor and acceptor molecules might be oriented stereospecifically within a benzene–maleic anhydride complex[11a]. This idea has now been supported by n.m.r. spectroscopic studies (with Dr. M. A. Hems). It is well known that the frequency at which a proton in a uniform magnetic field absorbs energy to pass from one spin state to another is related to the field strength. The field actually experienced by a proton is normally less than the applied field as a result of an opposing

secondary local field set up by induced circulation of orbital electrons. In a diamagnetically anisotropic solvent such as benzene, the field experienced by a proton will depend, *inter alia*, on its mean position in the magnetic field which results from induced electron circulation within the lowest energy $\pi$ orbital. Comparison of the chemical shifts of the vinylic protons of maleic anhydride relative to tetramethylsilane as internal standard in benzene and carbon tetrachloride has provided information on the preferred orientation of these protons relative to the benzene ring. (Carbon tetrachloride is used as the reference solvent because it is magnetically isotropic and has a dielectric constant similar to that of benzene.)

*Table 2* shows chemical shifts of the maleic anhydride protons calculated for three models, (VI), (VII), and (VIII), of a molecular complex with benzene over a range of interplanar separations. The measured chemical shift was 1·60 p.p.m. Comparison with related but stronger complexes for
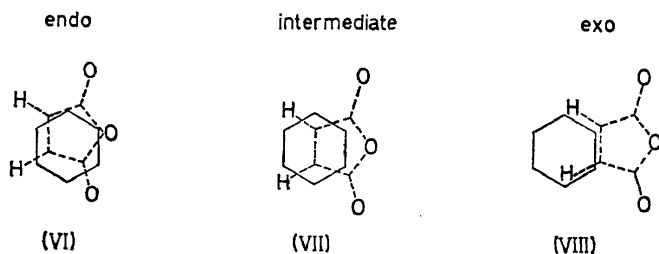


Possible models for a 1:1 benzene–maleic anhydride complex

*Table 2.* Calculated chemical shifts (p.p.m.) of the protons in maleic anhydride for models (VI), (VII), and (VIII)

| Interplanar distance (Å) | (VI) | (VII) | (VIII) |
|---|---|---|---|
| 2·09 | 0·23 | 1·63 | |
| 2·50 | 0·34 | 1·30 | 1·67 |
| 2·78 | 0·38 | 1·09 | 1·36 |
| 3·48 | 0·36 | 0·73 | 0·85 |
| 4·17 | 0·29 | 0·49 | 0·55 |

which x-ray measurements have been made would lead one to expect an interplanar separation of *c.* 3·0–3·5 Å; and the evidence mentioned earlier for an unusually large steric requirement for effective complexing between maleic anhydride and the benzene ring would appear to favour the lower of these figures, or even one slightly lower still. Examination of *Table 2* in the light of these considerations shows that the *exo* conformation (VIII) provides the best agreement with the experimentally measured chemical shift. An *exact* fit would require the unusually small interplanar separation of 2·55 Å; or put another way, an *exo* interplanar separation of 3·0 Å would have required a chemical shift of 1·17 p.p.m. It would probably be unreasonable to expect a closer agreement in view of the neglect of dipole-induced dipole effects in the treatment. Such effects would, according to some recent proposals[14], tend in any case to favour an *exo*- more than an *endo*-conformation for the complex.

This evidence for a preferred *exo* conformation within the complex is particularly interesting in the light of the previous evidence that photochemical charge-transfer excitation leads to formation of the adduct (III)[11] and that the 1,2-cycloaddition, long regarded as the initial bond-making step, has *exo* stereospecificity[9]. A possible relation of cause and effect can be seen. It might have been thought a general hypothesis that the preferred orientation within an intermediate unexcited complex should determine the stereochemistry of all cyclic photoaddition processes involving donor–acceptor systems, or at least those which occur in a concerted manner: it would not of course be essential for photoexcitation to involve a charge-transfer transition. But caution is necessary when considering a case where excitation of the complex is not synchronous with covalent bonding. The stereochemistry of the overall process should then be dependent on the orientation of the components within the excited complex, a matter on which n.m.r. studies are uninformative. There are indications that the addition of maleic anhydride to benzene provides such a case, as will be seen later.

## PHOTOADDITION OF MALEIMIDES TO THE BENZENE RING

Maleic anhydride, maleimide, and cyclopentene-2,4-dione (IX) form an isoelectronic triad, but of these only maleic anhydride and maleimide have been found to undergo either sensitized or unsensitized photoaddition to benzene (cf. refs. 15 and 16). The 2:1 adducts of maleimide or various *N*-substituted maleimides with benzene have structure (X) analogous to that of the maleic anhydride adduct (III), and have been synthesized from the
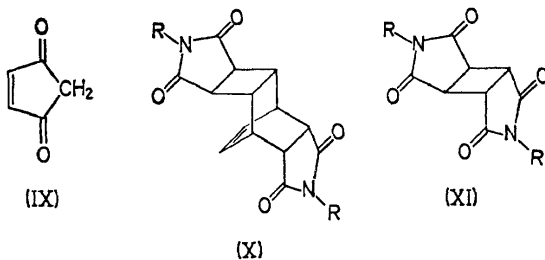


latter by conventional procedures. It is interesting however that the ease of addition of maleimides to benzene is markedly dependent on the nature of the group R attached to nitrogen. When R $=$ H, Bu$^n$, PhCH$_2$, 2-MeC$_6$H$_4$, or 2,6-Me$_2$C$_6$H$_3$, addition to give adducts of type (X) occurs quite readily, with or without benzophenone as sensitizer, whereas when R $=$ Ph, 3-MeC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, or 4-Bu$^t$C$_6$H$_4$, no unsensitized addition could be detected, and only traces of the adducts were obtained in sensitized reactions†. The main products from the latter sensitized

† These adducts are formed in very small amounts (1–10 mg h$^{-1}$ with a 500-watt medium-pressure mercury vapour lamp) and had not been detected at the time of a preliminary report[15].

reactions were *anti*-dimers of type (XI); but such dimers were not produced in the absence of benzophenone as sensitizer nor were corresponding dimers formed, with or without the sensitizer, from the first group of imides which readily gave 2:1 photoadducts with benzene.

These results provide an insight to the natures of the processes. It can be seen that those maleimides which add readily to benzene either have no $\pi$-electron system attached to the nitrogen atom or have a $\pi$-electron system which is prevented from overlapping significantly with the nitrogen *n*-orbital forming part of the $\pi$-electron system of the maleimide ring, either by the interposition of an insulating methylene group, as in *N*-benzylmaleimide, or by the presence of one or two *ortho*-substituents, as in *o*-tolylmaleimide and 2,6-xylylmaleimide†, which promotes a skew conformation of the benzene and maleimide rings. Thus in those *N*-arylmaleimides where relatively little hindrance to rotation about the *N*-aryl bond is present, coplanar and non-skew conformations of the two rings are possible and should make available excited states of the molecules having lower energies relative to those of molecules in skew conformations. It is suggested that the failure of these substituted maleimides to photoadd readily to benzene results from the functioning of these conformation-dependent low energy states as energy sinks. In principle, singlet and/or triplet species could be involved (see below), and inter- and/or intra-molecular energy transfer.

The foregoing proposal is supported by differences which we have observed in the ultraviolet absorption spectra of these maleimides. *Table 3* shows the values of $\lambda_{max.}$ and $\epsilon_{max.}$ for the longest wavelength absorption band.

*Table 3.* Ultraviolet absorption data for some maleimides (in cyclohexane)

| | $\lambda_{max.}$ (m$\mu$) | $\epsilon_{max.}$ | | $\lambda_{max.}$ (m$\mu$) | $\epsilon_{max.}$ |
|---|---|---|---|---|---|
| Maleimide† | 267 | 800 | *N*-2,6-Xylylmaleimide† | 288 | 620 |
| *N*-n-Butylmaleimide† | 297 | 760 | *N*-*o*-Tolylmaleimide‡ | 292 | 565 |
| *N*-Benzylmaleimide† | 297 | 670 | *N*-*m*-Tolylmaleimide§ | 324 | 425 |
| *N*-Phenylmaleimide§ | 322 | 435 | *N*-*p*-Tolylmaleimide§ | 330 | 400 |

† Colourless: photoadds readily to benzene.
‡ Very pale yellow: intermediate photoreactivity towards benzene.
§ Yellow: does not readily photoadd to benzene.

This band is attributable, following Matsuo[17], to an $n \rightarrow \pi^*$ transition in the carbonyl groups which is perturbed by a $\pi \rightarrow \pi^*$ transition of the imide ring in the increasing order *N*-aryl < *N*-alkyl < N—H: such perturbation accounts for the corresponding increase in intensity and to anomalous bathochromic shifts of $\lambda_{max.}$ with increased solvent polarity for maleimide and *N*-alkylmaleimides. It can be seen from *Table 3* that those maleimides which do not readily undergo photoaddition to benzene have $\lambda_{max.}$ at abnormally long wavelengths. Further, the absorption curves of

† 2,6-Xylylmaleimide shows reversible thermochromism consistent with higher conformational mobility of the xylyl group at higher temperatures.

these particular maleimides show pronounced tailing into the visible region, consistent with the existence of conformation-dependent low electronic energy levels. There does indeed appear to be a simple correlation between colour and photo-reactivity towards benzene in *N*-substituted maleimides (see *Table 3*).

## COMPLEXING OF MALEIMIDES WITH BENZENE:
## NATURE OF THE PHOTOEXCITED INTERMEDIATES

As previously discussed, photoaddition of maleic anhydride to benzene is known to involve a charge-transfer transition within a weak complex formed by the reactants[11]. The charge-transfer absorption is shown in *Figure 1*. Bradshaw reported that the absorption of maleimide in chloroform is unaffected by the presence of benzene (in chloroform) and concluded that no "charge-transfer complex" was likely to be involved in its photo-addition to benzene[16]. This conclusion illustrates the danger of relating spectroscopic properties observed in the presence of a solvent (e.g. chloro-form) to photochemical behaviour shown in its absence. Examination of very thin films ($5 \times 10^{-4}$ cm) of benzene solutions of maleimide and the *N*-substituted maleimides listed in *Table 3* has shown that the solute absorp-tion is indeed very similar to that found in chloroform solutions at wave-lengths longer than *c.* 280 m$\mu$; but abnormally strong absorption occurs at 230–280 m$\mu$, a range normally inaccessible with solvent benzene using cells of more conventional path length. Thus at 245 m$\mu$, $\epsilon_{apparent}$ is *c.* 2500 whereas the corresponding value for maleimide in chloroform is *c.* 250. The broad nature of the absorption band in benzene solution, and its intensity, strongly suggest that it results from a benzene→ maleimide charge-transfer transition within an almost wholly complexed species. Further, n.m.r. studies with maleimide similar to those with maleic anhydride described above have indicated a similar preferred *exo* or near-*exo* orientation of this solute with respect to benzene molecules. Thus maleimide appears to resemble maleic anhydride quite closely in its complexing behaviour, contrary to the previous report[16]. However, irradiation of maleimide and its *N*-substituted derivatives mentioned above in benzene at wavelengths > 280 m$\mu$ readily leads to the corresponding 2:1 adducts, and these conditions are very suitable for preparative experiments. In the case of maleimide itself, it is virtually impossible to decide whether one is exciting through the tail of a charge-transfer transition or through the tail of an $n \rightarrow \pi^*$ transition in free or complexed maleimide. But with the *N*-substituted maleimides, the positions and intensities of the $n \rightarrow \pi^*$ transitions in benzene solutions are very similar to those found in chloroform solutions, and the $n \rightarrow \pi^*$ bands are much better resolved from the charge-transfer bands than is the case with maleimide itself. These photoadditions to benzene clearly involve $n \rightarrow \pi^*$ transitions in the largely complexed *N*-substituted maleimides rather than charge transfer. In other words, photoadditions of *N*-substituted maleimides to benzene involve excited intermediates of a type different from that involved in the corresponding photoaddition of maleic anhydride. This mechanistic difference appears relevant to the further results now to be discussed.

# 1:1 INTERMEDIATES IN THE FORMATION OF 2:1 ADDUCTS OF MALEIC ANHYDRIDE AND MALEIMIDE WITH BENZENE

It was originally suggested that a 1:1 photoadduct (XII) is initially formed from maleic anhydride and benzene, and undergoes rapid 1,4-thermal addition of a second molecule of maleic anhydride[8]. This two-step mechanism appears to have been generally accepted by subsequent workers. Several analogies for the proposed initial 1,2-*exo* addition exist, e.g. 9,10-



(XII)          (XIII)          (XIV)          (XV)
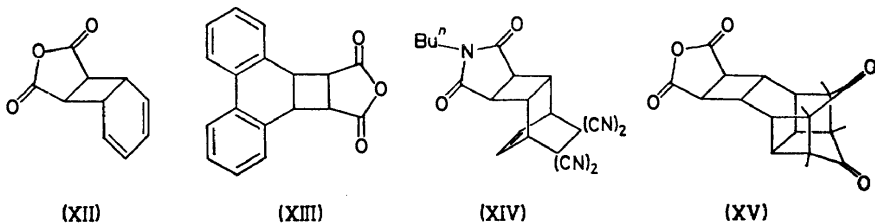
photoaddition of maleic anhydride to phenanthrene, giving 1:1 adduct (XIII)[18], 1,2-photoaddition of olefins to benzonitrile[12], and 1,2-photoaddition of acrylonitrile to benzene[19]. Yet all our attempts to isolate a 1:1 adduct (XII) have led only to the 2:1 adduct (III).

The use of tetracyanoethylene as a trapping reagent has provided helpful, if surprising, mechanistic information (Drs G. I. Fray and A. Gilbert). This compound was selected because it does not photoadd to benzene or maleic anhydride under normal conditions, does not markedly inhibit the photoaddition of maleic anhydride to benzene (other than by acting as an internal filter), and can be expected to have an approximately hundredfold rate advantage over maleic anhydride in capture of the cyclohexa-1,3-diene derivative (XII). In fact irradiation of benzene solutions of maleic anhydride and tetracyanoethylene, with and without benzophenone as sensitizer, led to the 2:1 adduct (III) as the only recognizable product: tetracyanoethylene was recovered almost quantitatively. On the other hand, the use of N-n-butylmaleimide in place of maleic anhydride led mainly to a new 1:1:1 adduct (XIV), together with traces of the usual 2:1 adduct (X; R = Bu^n). The conclusion seems inescapable that a 1:1 adduct of structure (XII) is *not* formed during the irradiation of maleic anhydride in benzene. In view of the evidence that the maleic anhydride–benzene complex is of the 1:1 type[20, 21] and that its excited forms (singlet and triplet) are precursors of the final 2:1 photoadduct (III)[11], one must conclude that the 2:1 photoadduct (III) results from reaction of a photoexcited benzene–maleic anhydride complex having charge-transfer character with an unexcited molecule of maleic anhydride or, less probably, the same unexcited complex. On the other hand, the production of a 1:1:1 adduct (XIV) from N-butylmaleimide, tetracyanoethylene, and benzene suggests that in this case, a conventional 1:1 adduct (XVI) may indeed be formed as an intermediate. It was noted above that $n \to \pi^*$ excitation within complexed N-butylmaleimide rather than charge-transfer is involved in the photoaddition of N-butylmaleimide to benzene. One is therefore led to conclude that the

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differing electronic characters of the excited species in additions of maleic anhydride and *N*-butylmaleimide to benzene may lead in the latter case



(XVI)          (XVII)          (XVIII)
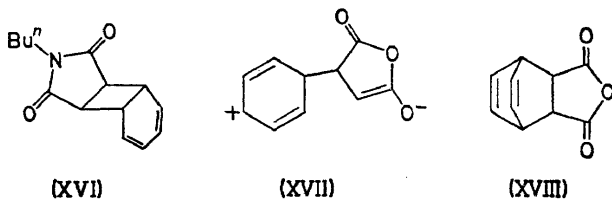
to an intermediate 1:1 adduct (XVI), and in the former case to the zwitterionic intermediate of which (XVII) represents a canonical form. It seems most probable that a *singlet* radical–anion/radical–cation pair would undergo extremely rapid combination in a poorly-solvating medium such as benzene: in contrast, a corresponding *triplet* pair formed (say) by energy transfer from triplet benzophenone should exist as an ion-pair. Thermal 1,4-addition of a second molecule of maleic anhydride to zwitter-ion (XVII) has an analogy in the reported formation of an adduct (XVIII) by thermal addition of maleic anhydride to benzenonium hexafluorantimonate[21a]. Evidently tetracyanoethylene is unable to replace maleic anhydride in the last stage, perhaps because it is a much weaker nucleophile than maleic anhydride. An analogous zwitter-ion mechanism can perhaps account for the surprising formation[13b] of a 1:1:1 photoadduct of duroquinone, maleic anhydride, and benzene (XV).

All the foregoing processes appear to occur by photoexcitation of the non-aromatic addenda, or by charge-transfer. Activation of the *aromatic* component of a system can lead to completely different varieties of chemical behaviour. These will now be considered.

## PHOTOISOMERIZATION OF BENZENE RING: IMPORTANCE OF ELECTRONIC AND VIBRATIONAL EXCITATION PROCESSES

The photoisomerization of liquid benzene at 55° to fulvene (XIX) *via* the first optical transition was originally reported in 1957[1]. Recently, benzvalene (XX) has been shown to be also formed under similar conditions, especially when the benzene is diluted by a paraffinic solvent[22]. Benzvalene



(XIX)     (XX)     (XXI)     (XXII)
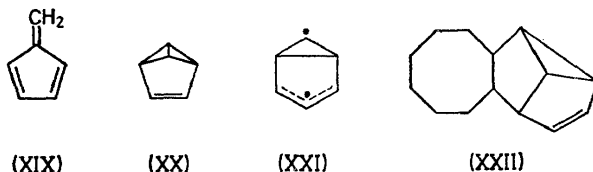
(XX) slowly reverts solely to benzene at room temperature[22], and there is as yet no definite evidence whether fulvene is wholly or only partly formed from it under photochemical conditions. The formation of both these isomers of benzene is promoted by increasing temperatures[1b, 22]. This

temperature effect is particularly marked in the formation of methylfulvenes and dibenzyl *via* the $S_1$ state of toluene at 60°: at 20° dibenzyl and other products are formed, but no traces of fulvenes[23]. These facts indicate that both electronic and vibrational excitation processes are involved in the isomerization of benzenes to fulvenes and benzvalenes, a conclusion which is further supported by the finding that the isomerization of benzene *vapour* to fulvene requires primary excitation *via* the second and/or third optical transitions (radiation of wavelength 1849 Å was used)[24]. It is to be expected that electronically excited levels higher than $S_1$ would very rapidly cascade down to produce $S_1$ molecules at high vibrational levels, from which isomers could be derived in the absence of the collisional activation available in the liquid phase: benzene is much more stable in the vapour than the liquid phase to irradiation at 2537 Å ($S_0 \to S_1$ transition)[25]†. The concept that chemical transformations of $S_1$ benzene occur only from upper vibrational levels ties in well with Noyes and Harter's recent report that the quantum yields of benzene fluorescence (i.e. for the process $S_1 \to S_0 + h\nu$) decrease markedly with decreasing excitation wavelength within the $S_0 \to S_1$ band[26], and with Braun, Kato and Lipsky's earlier observation that no ($S_1 \to S_0$) or other fluorescence occurs when benzene and some alkylbenzenes are excited directly to their $S_2$ states in either vapour or liquid phases[27] (cf. Ward's comparative studies on the photolysis of *p*-xylene vapour at 1600–2100 Å and 2537 Å[28]).

Molecular orbital considerations have suggested that the singlet diradical species (XXI), termed "prefulvene", is a precursor of both fulvene and benzvalene[29]. Orbital correlation diagrams show that the $^1B_{2u}$ state of benzene ($S_1$) can pass adiabatically into the electronic ground state of singlet prefulvene (XXI) by a 1,3-bonding process, but that the $^1B_{1u}$ state ($S_2$) cannot do so. It is a property of $^1B_{2u}$ benzene that carbon atoms $C_1$ and $C_3$ are non-bonding in the equilibrium molecular conformation (a regular, planar hexagon[2]), but tend to become bonding when brought closer together by distortions of the ring structure‡. The need for both vibrational and electronic components in the overall activation process follows accordingly. Singlet prefulvene is thought likely to be capable of brief independent existence because of the additional strain involved in its intramolecular cyclization to benzvalene, and because of evidence, to be discussed below, that it can be intercepted by olefins. In principle, the higher the vibrational level of the $^1B_{2u}$ benzene precursor (and other factors such as phase being equal), the more closely sequential would be the formation of the two new σ-bonds in benzvalene: the transformation could

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† $S_1$ Benzene produced by an intramolecular $S_2 \to S_1$ process would be vibrationally very "hot", and its rapid vapour-phase transformation to fulvene and benzvalene would probably generate "hot" forms of these. Thus the isolation of fulvene free from benzvalene following $S_0 \to S_2$ excitation of benzene could simply result from the known lower thermal stability of benzvalene than fulvene.

‡ 1,3-Bonding would result from a disrotatory twisting mode. The twist involved in any isomerization to *cis,cis,trans*-cyclohexa-1,3,5-triene ("Möbius benzene") would involve gross loss of symmetry, serious strain, and intermediate states of higher energy resulting from partial uncoupling of the π-electron system. "Möbius benzene" would not be electronically isoenergetic with $S_1$ benzene because of the different values of β appropriate to each. For these and other[30] reasons, we do not consider "Möbius benzene" to be a likely specific intermediate in the $S_0 \to S_1$ photochemistry of benzene, as in Farenhorst's interesting suggestion[31].

doubtless approach a concerted process at the extreme. But at the moderate vibrational levels of $^1B_{2u}$ benzene which would be attained under irradiation in the 230–270 m$\mu$ band at 20–80°, much of the observed chemical behaviour seems accounted for better in terms of prefulvene (XXI) than benzvalene (XX) as the key intermediate[30] (see also ref. 32 for some addition reactions which do seem to involve benzvalene intermediates).

## 1,3-PHOTOADDITION OF OLEFINS TO THE BENZENE RING

This strange process has been reported independently by two groups of workers[33, 34]. The addition of cyclo-octene to benzene occurs particularly readily, and leads mainly to the 1:1 adduct (XXII), together with c. 15 per cent of a second very labile 1:1 adduct†, and traces of cyclo-octylbenzene



(XXIII)          (XXIV)          (XXV)          (XXVI)
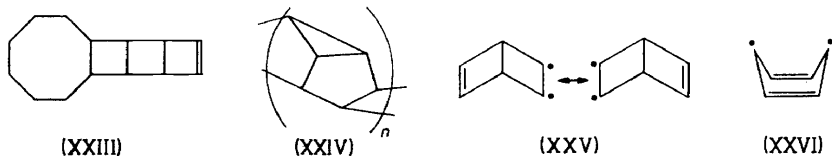
and other isomeric adducts[34]. The 1,3-adduct (XXII) can readily be prepared in quantities of 30–40 g at a time. The formation of such adducts can readily be explained through interaction of singlet prefulvene (XXI) with the olefin. The bond-making processes would be expected to be closely concerted (depending on the precise orientation of individual collisions); and there is indeed evidence that the original stereochemistry of the olefin is preserved in the 1,3-adducts[33]. At low olefin:benzene ratios, the main products are "ladder" telomers of benzene containing the repeating $C_6H_6$ unit (XXIV)[35]. Fulvene is not formed from benzene in the presence of olefins capable of 1,3-photoaddition, and is not a precursor of such adducts[34, 35].

According to these proposals, therefore, 1,3-photoaddition to olefins is a reaction closely related to the isomerizations to benzvalene and fulvene: all involve prefulvene (XXI) as a common intermediate, and all are expected to be singlet processes.

The role of triplet ($T_0$) benzene, of state $^3B_{1u}$, in photoaddition of olefins has not been clearly defined. Energy transfer to olefins seems to occur readily, and sensitization of *trans–cis* isomerization of but-2-ene *via* the triplet olefin provides the basis of Cundall's procedure for measuring the quantum yield for the formation of $T_0$ benzene[36]. One should not exclude the possibility that addition of $T_0$ benzene to a ground-state olefin is able to compete with energy transfer, but clearly such a process cannot in simple systems provide a major reaction pathway. It has been pointed out that isomerization of $^3B_{1u}$ benzene ($T_0$) to either or both of the triplet diradicals (XXV) and (XXVI) should be possible in principle[29]. Since we do not now believe that the adduct (XXIII) is a primary product of the photoaddition of

† This second adduct is readily thermally isomerized to the adduct previously thought to be a primary photochemical product and provisionally formulated as the cyclobutene (XXIII)[34]. Its lability has hindered the preparation of a pure specimen, and its structure is still uncertain. Yet another isomer is formed from it under acid conditions. Neither the primary nor the acid-isomerized isomer appears to be of structure (XXIII).

cyclo-octene to benzene, discussion of the possible participation of diradical (XXV) in this photoreacting system would not be fruitful at the present time†. Analogues of this triplet diradical can however be considered as reasonable intermediates in such processes as the photochemical formation of "hexafluoro-Dewar-benzene" (XXVII) in the vapour-[37] but not
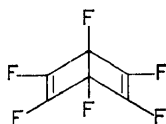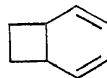


(XXVII)          (XXVIII)

the liquid-phase[38], the formation of a photoadduct of hexafluorobenzene and cyclo-octene[34], and the photoisomerization of tri-t-butylbenzenes to prismanes[39]. If adducts of aromatic compounds with olefins were arising mainly by photoaddition of "Dewar-benzene", prismane, or benzvalene isomers, two photochemical stages would be required, and considerations of the optical filtering effect in a system containing an excess of the aromatic species suggest that the second stage would need to involve some kind of photosensitization: for this, absorption curves seem to rule out the possibility of singlet–singlet energy transfer from the aromatic species to any of its valence-bond isomers, and corresponding triplet–triplet energy transfer processes would normally be competing disadvantageously with those involving the initial olefin. The proposed one-quantum steps involving diradical species avoid mechanistic difficulties of this type.

The triplet "boat" diradical (XXVI) was originally proposed to account for the observed *para* 1,4-photoaddition of 1,3-dienes to benzene[40]‡, and also represents a type of species capable in principle of transformation into "Dewar-benzenes". Its formation from benzene appears to be promoted by ammonia, primary-, secondary-, and tertiary-amines. Thus, cyclohexylamine[41], piperidine[41], and pyrrole[42] give the adducts (XXIX), (XXX), and (XXXI) respectively, together with a dihydrodimer of benzene having properties consistent with structure (XXXII), and identical with a product

† Srivinasan and Hill have described an adduct of analogous structure formed from cyclobutene and benzene[36a]. If this is a primary photochemical product, diradical (XXV) could well be involved. Alternatively, its formation in a two-step process *via* (XXVIII) needs to be considered—but see below.

During discussions, Dr L. Kaplan stated that he had experimentally confirmed that benzvalene is not a precursor of the 1,3-adducts of olefins and benzene. This finding, coupled with a previous report[34] that fulvene is not such a precursor, supports the present proposal that the photoisomerization of benzene to benzvalene is a non-concerted process involving prefulvene (XXI) as an intermediate, interception of which by an olefin leads to the 1,3-adducts such as compound (XXII).

Professor R. Srinivasan stated that there is now some doubt whether an adduct of structure



is really formed from cyclobutene and benzene (cf. ref. 36a); but 1,3-addition does occur in this case.

‡ A two-stage mechanism involving addition of $T_0$ diene to $S_0$ benzene can also be envisaged for this type of process. The diradical (XXVI) would be expected to be capable of fairly rapid conformational inversion through a planar or near-planar state—the diagrams herein exaggerate its probable degree of non-planarity.

of the Birch reduction of biphenyl. Discussion of mechanistic details would be premature at this stage, but the formation of compounds (XXIX)–(XXXII) appears most readily explicable on the basis of diradical (XXVI) or the derived monoradical (XXXIII) as common key intermediates.



(XXIX)        (XXX)        (XXXI)

(XXXII)        (XXXIII)
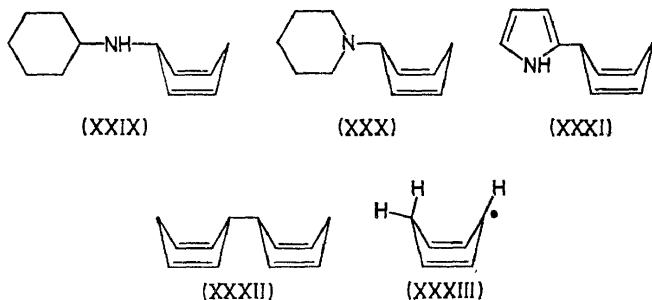
The foregoing proposals are summarized in *Figure 3*. They are intended to provide a mechanistic framework which can support a broad range of existing experimental observations and be tested against future results. Many
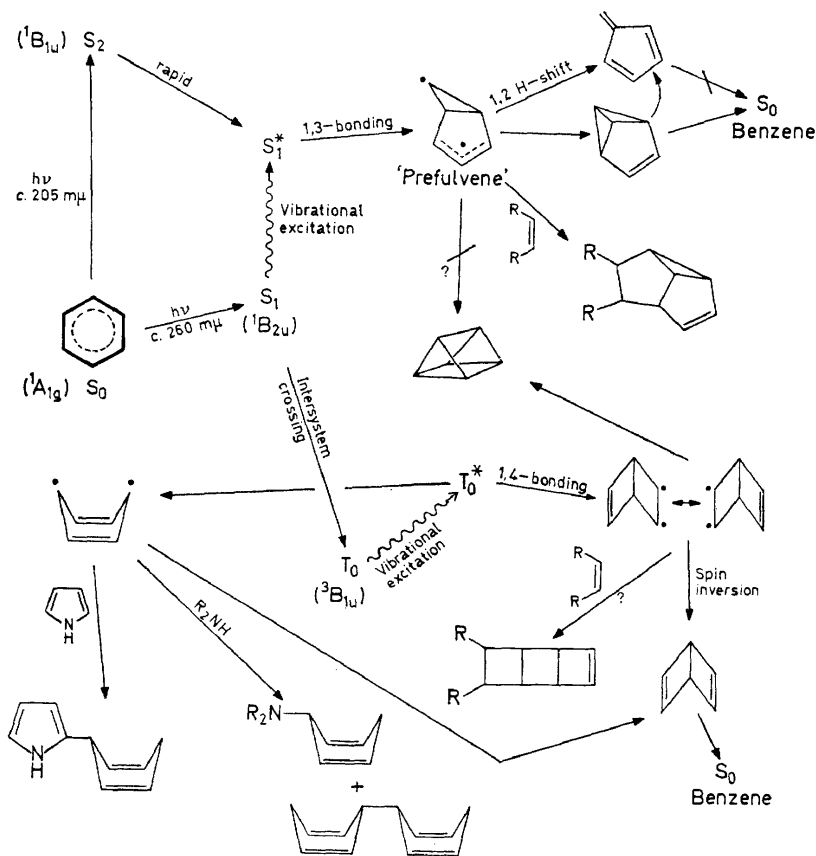


*Figure 3*. Proposed reactive intermediates formed from $S_1$, $S_2$, and $T_0$ states of benzene

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details will need to be filled in, for example the rôle played by excimers and exciplexes involving excited aromatic molecules. Extensions to cover related acid-catalysed processes have been made[30], but discussion of these is reserved for a future occasion.

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### Note added in proof

It follows from *Figure 3* and the M.O. symmetry relationships discussed in ref. 29 that 'Dewar-benzene' should result from $B_{1u}$ benzene species, but not from those of $B_{2u}$ symmetry. Dewar-benzene could not be formed in a one-step process from $S_1$ benzene, but it should be so formed from $S_2$ benzene, of state $^1B_{1u}$. Dr. H. R. Ward (private communication) has now demonstrated that Dewar-benzene is indeed formed by irradiation of liquid benzene at *c.* 2000 Å $(S_0 \rightarrow S_2$ transition), but not at 2537 Å $(S_0 \rightarrow S_1$ transition), in gratifying confirmation of the theoretical proposals[29]. The survival of Dewar-benzene in the liquid, but not vapour-phase $S_0 \rightarrow S_2$ irradiations of benzene can be attributed to rapid collisional deactivation of this thermally labile substance from high initial vibrational levels in the relatively thermally cool liquid phase.

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