Stereochemical Control in *meta* Photocycloaddition of Alkenes to the Benzene Ring: the Anomalous Behaviour of Cyclohexene

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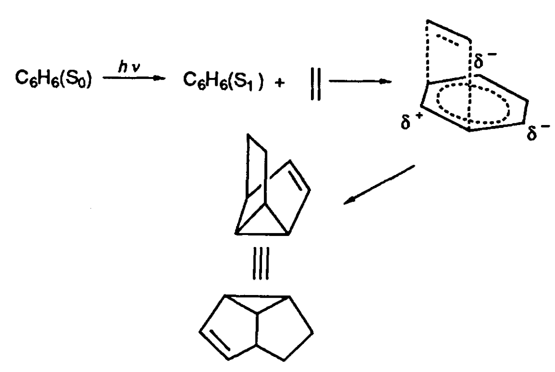
The intermolecular *meta* photocycloaddition of cycloalkenes to benzenes occurs with marked *endo* stereoselectivity, although the *exo* process would be favoured on purely steric grounds. Additions normally occur 2,6 to monoalkylbenzenes, but increasing the size of the alkyl group in the order Me, Pr^i, Bu^t leads to an increasing tendency for 3,5-addition without significant loss of the *endo* stereoselectivity. These effects are attributed to a weak but orienting interaction between the α-CH in the alkene and the S_1 state of the aromatic species: this is termed 'intermolecular hyperconjugation'. In the bichromophoric system **14b**, models show that only an *endo* orientation is feasible, but that this is subject to steric hindrance resulting from unfavourable orientations of the α-methylene groups in the cyclohexenyl ring: hence the low quantum efficiency of the *meta* addition process, in contrast with the relatively efficient *endo* process in the cyclopentene **14a** where there is no analogous steric effect. In compounds **15a** and **15b**, only an *exo* orientation between the cycloalkene moiety and the aromatic ring is sterically feasible. Accordingly, the *meta* cycloadditions are stereospecifically *exo*, and occur with comparable quantum yields for the cyclohexene and cyclopentene derivatives. The anomalously low reactivity of cyclohexene in *meta* photocycloaddition to benzene applies only to the normally favoured *endo* process, and is attributable to sterically unfavoured 'chair' conformations of the cycloalkene.

The *meta* photocycloaddition of alkenes to benzenes has attracted considerable interest since the first reports of the process in 1966.[1,2] The synthetic potential of both the inter- and intra-molecular process has been elegantly demonstrated by Wender and co-workers[3] but the elucidation of the mechanistic details of the process[4] and factors which can be used to induce selectivity into isomer formation[5,6] continue to be active areas of research. It is now widely accepted that the reaction proceeds from the first excited singlet state of the arene. Although the involvement of an excited state complex (exciplex) between the addends appears to be involved in some cases,[7] for the benzene–cyclopentene system the addition is deduced to proceed in one step by direct attack of the alkene onto the arene.[8] The observed control of the regiochemistry of the addition by substituents on the arene is considered to reflect their abilities to stabilise developing fractional charge centres in preferred addend orientations. This rationalisation is strongly supported by semi-empirical calculations which show that on approach of the alkene, the benzene ring becomes polarised as shown in Scheme 1.[9] Such polarity features can also be used to rationalise the *exo* stereoselectivity of the addition of dioxoles to benzene and anisole.[10] An *exo* approach in these systems leads to an electrostatic attraction between the oxygen atoms of the dioxole and the developing positive charge on the carbon whereas there is a repulsive interaction with the anionic allylic moiety for an *endo* orientation. Furthermore, dioxoles have no α-CH groups that might tend to promote *endo* addition.[11,12]



Scheme 1

We have observed that the regiochemistry of the *meta* photocycloaddition of ethenes to alkylbenzenes is very dependent on the size of the arene substituent.[11] For example, the expected 2,6-addition is essentially the sole route for the reaction of *cis*-cyclooctene and toluene, but with *tert*-butylbenzene two *meta* cycloadducts are formed in a 1 : 1.5 ratio reflecting 2,6- and 3,5-attack of the alkene, respectively. Furthermore both these adducts have *endo* stereochemistry[12] in contrast to the *exo* stereochemistry expected on steric grounds. These findings were interpreted in terms of the steric interaction between the substituent and the alkene inhibiting the 2,6-attack, but we proposed that the *endo* stereochemistry arises from a novel intermolecular bonding interaction, hyperconjugative in type, between the α-hydrogens on the alkene and the S_1 arene.[12,13] This interaction, although weak, is sufficient to align preferentially the addends in a sandwich (*endo*) orientation **1** regardless of the regiochemistry of the approach. We termed this phenomenon 'intermolecular hyperconjugation'. Subsequently, Cornelisse *et al.* described evidence for developing fractional negative charge in the region of the S_1 arene proximate to the allylic hydrogens:[4a,8,9] they proposed the term 'anionic hyperconjugation' in which there is a small degree of electron donation from the benzene ring to the ethene α-C–H bonds.[14] In the present paper we present the details of our preliminary reports[11,12] and consider how this weak *endo* orienting effect may account for the anomalous and hitherto unexplained low reactivity of cyclohexenes relative to other cycloalkenes in *meta* cycloadditions.[15]

Results and Discussion

meta *Addition to* p-*Cymene*.—Our interest in the *meta* photocycloaddition of alkenes to alkylbenzenes stemmed from a need to assess not only mechanistic aspects, including the directing influence of substituents, but also the potential of the process as a ready route to various natural products, *e.g.* α-

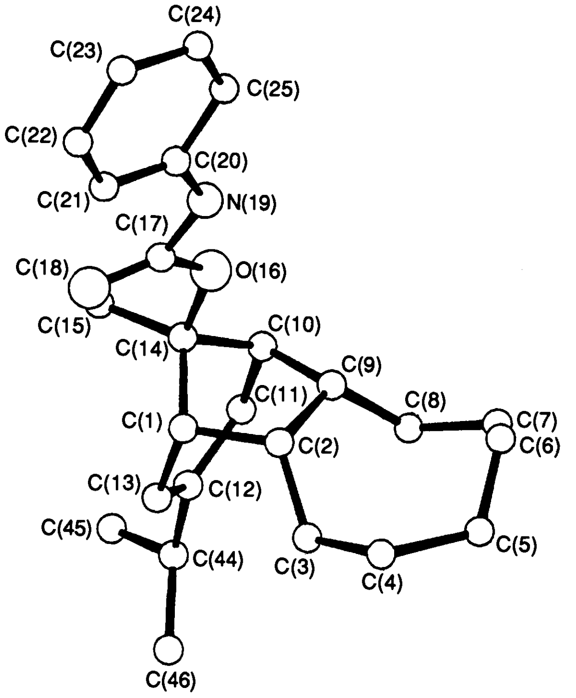
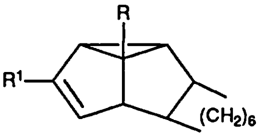


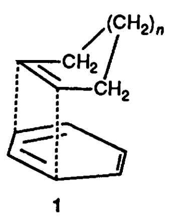
Fig. 1

thujene derivatives. For thujene synthesis, it was originally expected that steric factors in an *endo* approach of an alkene, as in the additions to benzene, would favour addition to the 2,6-positions relative to the 2′-propyl group. Thereby, bridged α-thujene analogues might conveniently be synthesised. This expectation concerning the regioselectivity of the addition proved to be unjustified but valuable insights into the factors which control the orientation of the addends were obtained.

Irradiation of *p*-cymene in equimolar amounts with (*Z*)-cyclooctene, either neat or in solvents of varying polarity, gave one 1 : 1 adduct with 95% selectivity. The adduct was assigned a 1,3-disubstituted *meta* structure of type **2** by ^{1}H NMR spectroscopy. Surprisingly, the chemical shifts of the methyl protons were inconsistent with the expected 3-methyl-1-(2′-propyl) structure but rather showed that addition had occurred 2,6- to the methyl group to give the 1-methyl-3-(2′-propyl) isomer. Neither these spectral data nor those of analogous adducts from other cycloalkenes allowed totally unambiguous determination of the stereochemistry, so X-ray crystallographic determination was undertaken. Crystalline derivatives of *meta* photocycloadducts can be obtained from the addition of dienophiles to the ethenylcyclopropane system (homo-Diels–Alder reaction) or by protonation and ring opening to give alcohols.[16] For the adduct of *p*-cymene and *cis*-cyclooctene, suitable crystals for analysis were obtained by the latter procedure followed by reaction of the alcohol (feathery needles) with phenyl isocyanate. The phenylurethane was assigned *endo* stereochemistry from X-ray crystallographic analysis. The structure consists of discrete molecules of **3**. As stated in the experimental section, three of the carbon atoms are disordered over two sites, but Fig. 1 shows an ordered molecule. The five-membered ring has an envelope conformation with C(14) 0.72 Å from the plane of C(1), C(2), C(9) and C(10). The six-membered ring is similarly folded with C(14) 0.85 Å from the plane of C(1), C(10), C(11), C(12) and C(13). The cyclooctane ring is disordered at C(5) and C(6), the two atoms furthest from the C(2)–C(9) bridge. The benzene ring is twisted by 12.5° from the plane of N(19), C(17), O(16) and O(18). There is an intermolecular hydrogen bond between the NH group and the carbonyl oxygen O(18)$\cdots$N(19) ($-0.5 + x$, $-0.5 + y$, z 2.98 Å). From the assignment of **3** to the urethane, the alcohol and the *meta* photocycloadduct are unequivocally deduced to have *endo* stereochemistry as shown in **4** and **5** respectively. The regiochemistry of the addition does not therefore arise simply from steric effects of the bulky 2′-propyl group, whereby the *endo* oriented alkene is displaced towards the 3,5-positions (2,6-relative to the methyl group), for this would have led to an *exo* adduct. Clearly there must be some attractive interaction between the cycloalkene and the S$_1$ benzene which occurs only in an *endo* orientation.



5 R = CH$_3$, R^1 = CH(CH$_3$)$_2$
7 R = CH$_3$, R^1 = H
8 R = H, R^1 = CH$_3$
9 R = CH(CH$_3$)$_2$, R^1 = H
10 R = H, R^1 = CH(CH$_3$)$_2$
11 R = C(CH$_3$)$_3$, R^1 = H
12 R = H, R^1 = C(CH$_3$)$_3$



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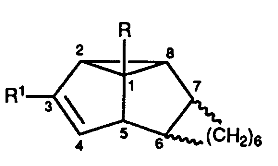

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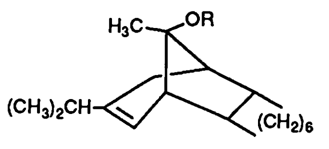
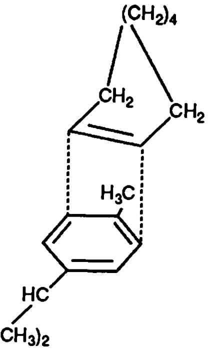


3 R = CONHC$_6$H$_5$
4 R = H



6

Three effects need to be considered: (*a*) steric effects of substituents on the arene, (*b*) the possibility of favouring *endo* addition by intermolecular hyperconjugation and (*c*) the ability of a substituent on the arene to stabilise an incipient positive charge on C(1) as 2,6-bonding to the alkene develops. The established structure **5** could possibly result from either a significant degree of steric repulsion from the Me group in the orientation **6** when the alkene approaches 2,6-*exo*, and/or stabilisation of *endo* orientation by factor (*b*). The relative importance of these is far from obvious. The preference for 2,6- rather than 3,5-*endo* addition might likewise result from either a differential steric effect and/or lower ability of 2-propyl than methyl hyperconjugatively to stabilise the development of incipient positive charge on positions 4 and 1 respectively. Again, the relative importance of these factors is hard to gauge in the absence of further data, although for reasons derived from the study of monoalkylbenzenes described previously,[11,12] we suspect that the former factor is the more important.

Table 1 Efficiencies of *meta* photocycloaddition of (*Z*)-cyclooctene to alkylbenzenes.[a] Reaction products are in parentheses.

Position of addition	Arene Toluene	2-Propylbenzene	*tert*-Butylbenzene
2,6-[b]	1.30 (**7**)	0.4 (**9**)	0.18 (**11**)
3,5-[c]	0.03[d] (**8**)	0.2 (**10**)	0.26 (**12**)

[a] Values relative to 1.0 for the *meta* photocycloaddition of (*Z*)-cyclooctene to benzene; 1.0 mol dm^{-3} arene, 3.5 mol dm^{-3} (*Z*)-cyclooctene in cyclohexane. [b] This yields the 1-substituted adduct. [c] This yields the 3-substituted adduct. [d] Estimated from the mixture of alcohols produced on acidolysis.[16]

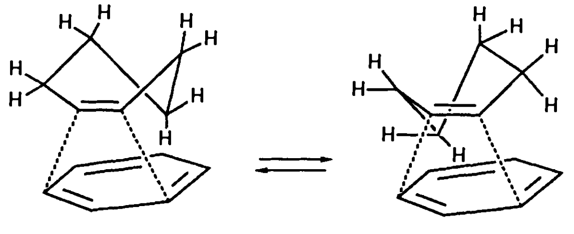
meta Cycloadditions to Monoalkylbenzenes.—To assess the relative importance of the above three directing influences in *meta* cycloadditions, and to determine whether the *endo* orienting effects of the addends would be maintained for both 2,6- and 3,5- modes of addition, we investigated the photocycloaddition of (*Z*)-cyclooctene to toluene, 2-propylbenzene and *tert*-butylbenzene. The results are presented in Table 1. The *meta* adducts **8**, **10** and **12** provide the first examples of formation of 3-monosubstituted derivatives. Two conclusions follow from these data. Firstly, the methyl group in toluene slightly activates the ring relative to benzene. This effect can be rationalised in terms of hyperconjugative stabilisation of incipient positive charge on C(1), and is relatively uncomplicated by steric factors. Secondly, the effect of increasing substituent size is mainly to decrease the efficiency of 2,6-addition: the efficiency of 3,5-addition is largely independent on 2-propyl and *tert*-butyl substituent sizes (the datum for 3,5-addition to toluene should be regarded as qualitative only).

The *endo* stereochemistry of the 2,6-addition regioisomers was assigned from comparison of their ^{1}H NMR spectra with those reported for other 1-substituted *meta* photocycloadducts.[17] In particular the $J_{5,6}$ values of the order of 6 Hz are characteristic of *endo* adducts whereas for the corresponding *exo* isomers this coupling is very small or zero. The adducts from 3,5-attack could be similarly assigned *endo* stereochemistry. Formation of these 3-substituted adducts is sterically much less favoured (in contrast to the 2,6-reaction) than that on the corresponding *exo* isomers, but the stereochemical assignment was confirmed by X-ray crystallography.[12]

Hence, regardless of the regiochemistry of the reaction and despite unfavourable steric interactions in some orientations, the stereochemistry of *meta* photocycloaddition of (*Z*)-cyclooctene to alkylbenzenes is highly selectively *endo*. Similar results have been observed with cyclopentene as the alkene both by ourselves and, more extensively, by others.[5] (*E*)-Di-*tert*-butylethene does not yield photoadducts with benzenes[15] though this may be due to steric effects and/or the absence of α-H atoms). Clearly the origins of the present *endo* orienting effect do not involve the C=C bond of the alkene but must result from interactions between the S_1 arene and the allylic hydrogens. As noted in the Introduction, we consider that this weak but stereochemically important interaction involves a minor degree of electron donation from an allylic $-CH_2-$ group orbital into the lowest partly filled orbitals of the S_1 arene.[12] Recently, however, it has been reported that as the addends approach, polarity develops in the electronically excited benzene ring as shown in Scheme 1:[9] the allylic methylenes are then positioned over a region of fractionally increasing electron density. For this to result in a bonding interaction sufficient to account for the *endo* stereospecificity, one can envisage the induction of coulombic attraction between α-CH_2 and the δ^- moiety of the benzene ring. Alternatively a degree of charge transfer between these moieties may occur, in the transition state or an exciplex, either from the ring to an antibonding group orbital on CH_2, or from a bonding group orbital to antibonding orbitals on the ring—intermolecular hyperconjugation as we have termed it. Any explanation based on purely coulombic attraction encounters the problem of explaining why *endo* stereoselectively requires the presence of α-hydrogens on the alkene. Further, any idea of hydrogen bonding between the α-hydrogens and the δ^- moiety of the ring also raises serious conceptual difficulties. Electron transfer to the α-hydrogens[14] would presumably have to involve an antibonding group orbital, yet such an orbital would be a very poor acceptor—much poorer than ψ_2 of an alkene for example. Yet when an ethylenic bond is also present to act as an electron acceptor, as in *meta* photoaddition of cyclohexa-1,4-diene to benzene, *endo* stereoselectivity is lost: the *endo*/*exo* ratio is *ca.* 1.0.[18] These considerations leave one with the original proposal that *endo* orientation is probably better thought of as resulting from a degree of electron transfer of hyperconjugative type from a group orbital on CH_2 to antibonding orbitals of S_1 benzene, notwithstanding the development of fractional negative charge on the 3,5-positions of the ring concurrently with 2,6-bonding to the alkene.

The Case of Cyclohexene.—Cyclohexene as a *meta* addend has long been anomalous in comparison with other cycloalkenes and acyclic alkenes.[15,19] The *meta* photoadditon to benzene occurs with a low quantum yield ($\varphi_{exo+endo}$ = 0.03, *cf.* 0.25 for the addition of cyclopentene) and the *endo*/*exo* ratio is 2 which is again unexpectedly low (*cf.* the value of *ca.* 8 for the addition of cyclopentene). At high benzene concentrations, cyclobutane dimers of the cyclohexene are the main products: these appear to result from triplet cyclohexene which itself arises from triplet benzene formed by dissociation of its excimer,[20] but other alkenes give only traces of such dimers even at high benzene concentrations.

From inspection of molecular models it is evident that a close approach of cyclohexene to the benzene ring in an *endo* orientation is much more sterically hindered by the preferred conformation of the cycloalkene than is the case with other cycloalkenes. Thus, as shown in **13a**, **b**, the preferred *endo* alignment of the molecules inevitably results in one of the β-methylene groups of the cyclohexene inhibiting the proximity required for bonding between the addends. Note that this steric effect persists in all 'chair' conformers of the cyclohexene ring: it accounts for the low efficiency of *endo* cycloaddition. On the other hand, *exo* addition does not have this steric requirement, so it is satisfying to find that the quantum yields of *exo* addition of cyclohexene (0.01) and cyclopentene (0.025) are of the same order. However, these differences, although minor, are probably real, since the quantum yields for analogous *exo meta* cycloadditions of cycloheptene and (*Z*)-cyclooctene are 0.11 and 0.07 respectively.[15] The factors governing the efficiencies of *exo meta* photoadditions are not yet understood.

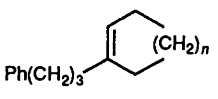


13a **13b**

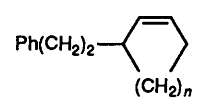
In systems where the cyclohexene is forced to approach in an *exo* orientation, we reasoned that *meta* cycloaddition should occur with increased efficiency. Such restricted orientation of the addends can be built into the system by linking the chromophores. We have recently reported the results of 254 nm

Table 2

Bichromophore	Preferred orientation of approach	Photochemical product
14a	*endo* 2,6- and 1,3-	2,6-*endo* and 1,3-*endo* addition → **16**, **17** and **18** in respective relative yield of 1:1:0.5 ($\varphi_{total} = 0.21$)
14b	*endo* 2,6- and 1,3-	2,6-*endo* addition → **19** ($\varphi = 0.03$) + 9 minor photoisomers
15a	*exo* 2,6- and 1,3-	2,6-*exo* and 1,3-*exo* addition → **20** and **21** in respective relative yields of 9:1 ($\varphi_{total} = 0.12$)
15b	*exo* 1,3- more likely than *exo* 2,6 as a result of the proximity of benzylic and β-methylenic hydrogens	1,3-*exo* addition → **22** and **23** in respective relative yields of 1.35:1.00 ($\varphi_{total} = 0.15$)

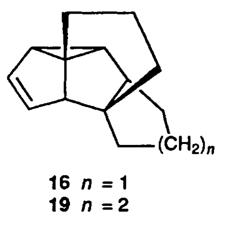


14 a; $n = 1$
b; $n = 2$

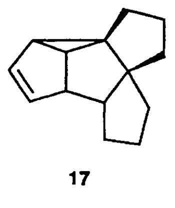


15 a; $n = 1$
b; $n = 2$

irradiation of some phenylcyclopentenyl and phenylcyclohexenyl bichromophores,[21] and we now extend and re-examine these observations. In all cases a C_3 chain was used to separate the arene and alkene moieties since it is well-known that a link of three units maximises both the extent of interaction and photochemical reaction efficiency of the chromophores in non-conjugated bichromophoric systems. Molecular models show that for the 1-cycloalkenylphenyl compounds **14** interaction of the chromophores can only occur in an *endo* (sandwich) orientation. Either a 1,3 or 2,6 approach of the alkene to the phenyl group is feasible, but for the cyclohexenyl compound, the interaction is clearly inhibited by the β-methylene group, as in the intermolecular case. In contrast, the 2-cycloalkenylphenyl systems **15** must take up an *exo* orientation in order that the chromophores may interact. These preferred orientations and the results of 254 nm irradiation of 1% w/v solutions of the bichromophores are shown in Table 2. To summarise: when an *endo* orientation is imposed, cyclopentene adds much more efficiently than cyclohexene, but when an *exo* orientation is imposed, both cyclopentene and cyclohexene add quite efficiently and with comparable quantum yields. Moreover, the enforced *exo* intramolecular *meta* cycloadditions of **15a** and **15b** occur with quantum yields similar to that ($\varphi = 0.15$) for the reaction with 5-phenylpent-1-ene where conformational restraints on the orientation are absent.[21,22]



16 $n = 1$
19 $n = 2$



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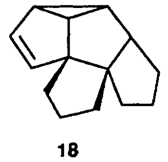

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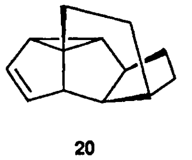

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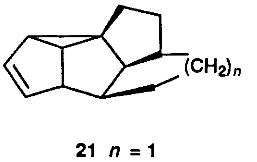
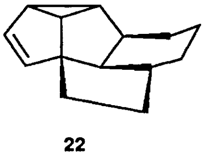


21 $n = 1$
23 $n = 2$



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Experimental

Photochemical and Analytical Methods.—Irradiations (254 nm) were of equimolar mixtures of the arene and alkene either neat or in cyclohexane or acetonitrile solutions (1.0 mol dm^{-3} of each addend) in 50 × 1 cm silica tubes using two 60 cm 30 W low pressure mercury arc lamps. The bichromophores **14a**, **b** and **15a**, **b** were irradiated as 1% w/v solutions in cyclohexane in a similar apparatus. Nitrogen degassing of solutions gave cleaner reaction products but did not appreciably influence the reaction efficiency: periodic cleaning of the irradiation tubes greatly increased the yields from preparative experiments. Quantitative determinations of the intermolecular additions relative to the benzene-(*Z*)-cyclooctene system and of the intramolecular additions relative to 5-phenylpent-1-ene were carried out in 10 × 1 cm tubes in a merry-go-round holding eight such tubes. 2,2,4,4,6,8,8-Heptamethylnonane was used as an internal GC standard for quantitative experiments.

The reactions were monitored by GC using a Hewlett–Packard 5790A instrument fitted with a flame ionization detector and a 12 m BP1 (OV1 equivalent) bonded phase capillary column. Separation and purification of the photoproducts were achieved by either flash chromatography on ICN silica 32–63 (Park Scientific Ltd.) or by preparative GC using a Perkin-Elmer F-21 fitted with a 100 × 6 mm i.d. stainless steel column packed with 15% w/w Carbowax 20M or 20% Apiezon L on 80–100 mesh Universal B support. NMR spectra were recorded on a JEOL FX90Q or Bruker WM250 instrument with tetramethylsilane as internal reference and in $CDCl_3$ solution except where otherwise stated. IR spectra were obtained using a Perkin-Elmer 1420 spectrophotometer and accurate mass data were recorded on a V.G. Miocromass 70-70 Spectrometer (Harwell) and a Kratos MS80F instrument at the Tate and Lyle Research Centre (Reading). The necessary purity of the sample for accurate mass data was assured in each case by capillary column GC and by TLC (Camlab Polygram G/UV precoated sheets). Elemental analyses were performed by the Chemistry Department, The City University.

Crystallography.—The *endo* stereochemical assignment of **12** by X-ray crystallography is reported in ref. 12. Crystal data for **3**, $C_{25}H_{35}NO_2$, $M = 381.3$, orthorhombic, spacegroup *Pbca*, $a = 12.868(9)$, $b = 9.210(7)$, $c = 36.610(17)$ Å, $U = 4338.8$ Å^3, $Z = 8$, $F(000) = 1664$, $dm = 1.20$ g cm^{-3}, $dc = 1.17$ g cm^{-3}, MoKα radiation ($\lambda = 0.7107$ Å), μ(MoKα) $= 22.4$ cm^{-1}.

A crystal of **3** of approximate size 0.3 × 0.3 × 0.3 mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer and data were collected *via* variable width ω scan. Background counts were for 20 s and a scan rate of 0.0333° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$.

1899 independent reflections with 2θ max of 50° were measured on a diffractometer, of which 1262 with $I > 2\sigma(I)$ were used in the calculations. The structure was solved by statistical methods. Two carbon atoms in the cyclooctane ring and one of the isopropyl carbon atoms were disordered almost equally over two sites. For each pair occupancy factors were refined but constrained to add up to 1.0. All ordered C, N, O atoms were refined anisotropically, disordered C atoms were refined isotropically, as were hydrogen atoms. Methyl hydrogen atoms were refined as rigid groups while other hydrogen atoms were placed in calculated positions. Hydrogen atoms on disordered atoms were not included.

The structure was given a weighting scheme in the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R values were 0.073 (R_w = 0.084). In the final cycle of refinement all shifts were less than 0.10σ. In the final difference Fourier map, the maximum, and minimum heights were 0.28 and −0.27 e $Å^{-3}$ respectively. Calculations were carried out using SHELX76 and some of our own programs on the Amdahl V7 at the University of Reading.

Photoproducts.—The spectral features which allow unambiguous structural determinations of the inter- and intramolecular photocycloadducts of arene–alkene systems to be made are given fully in refs. 4(*a*), 5, 6, 17, 19 and references therein. Thus only the structurally relevant ^1H NMR data for the photoproducts are presented here. All coupling constraints are in Hz.

(a) p-*Cymene and* (Z)-*cyclooctene.* Irradiation of an equimolar mixture (100 cm^3) of the addends for 24 h with periodic cleaning of the quartz tubes gave after vacuum distillation (0.05 mm Hg, 140 °C) a pale yellow oil (3 g) of essentially one component (*ca.* 95% purity). Cycloadduct **5** δ_H 5.13 (4 H, br s), 2.42 (5-H, 6-H, 7-H, overlapping multiplets, $J_{5.6}$ 6.7, $J_{6.7}$ 7.0), 1.34 (3 H, s, CH_3), 1.09 (6 H, d, CH_3) and 2.2–1.0 (2-H, 8-H, 2-propyl-H, cyclooctane protons, overlapping m's). The conversion of **5** to the alcohol **4** and the spectral data for **4** are given in ref. 16. The phenyl urethane **3** was obtained by refluxing **4** (0.3 g) in hexane (10 cm^3) in the presence of a 10% molar excess of phenyl isocyanate for 30 min. Recrystallisation from ethanol gave 0.4 g of **3** m.p. 189.5–191 °C; δ_H 7.50 (2 H, d), 7.36 (2 H, d), 7.21 (1 H, overlapping dd's), 6.65 (1 H, br, s), 5.44 (1 H, br d), 4.26 (4 H, overlapping m's), 2.71 (1 H, m), 2.58 (1 H, m), 1.69 (3 H, s, CH_3), 1.01 (6 H, d, CH_3) and 1.7–1.0 (13 H, overlapping m's); ν_{max}(Nujol) 1710 (s), 1690 (m) cm^{-1} (Found: C, 78.93; H, 9.45; N, 3.25%. $C_{25}H_{35}NO_2$ requires C, 78.74; H, 9.19; N, 3.67%).

(b) *Toluene and* (Z)-*cyclooctene.* Irradiation of an equimolar mixture (100 cm^3) of the addends for 24 h gave 5 g of a pale yellow oil after vacuum distillation (0.1 mm Hg, 140 °C). The adduct **7** comprised *ca.* 95% of the product mixture and was identified by comparison of its spectral data with those reported in ref. 23. The acidolysis products of **7** were obtained as outlined in ref. 16.

(c) 2-*Propylbenzene and* (Z)-*cyclooctene.* The two major 1:1 adducts (ratio 2:1; *m*/*z* 230 (M^+); 3.5 g from irradiation of 100 cm^3 of an equimolar mixture of the addends for 36 h) were separated by preparative GC. **9** δ_H 5.72 (3-H, dd, $J_{2.3}$ 2.0, $J_{3.4}$ 5.5), 5.58 (4-H, dd, $J_{4.5}$ 2.5), 2.79 (5-H, m, $J_{5.6}$ 6.0), 2.42 (3 H, 6-H, 7-H and 2-propyl-H, m, $J_{7.8}$ 6.5), 0.93 (6 H, d, CH_3) and 1.90–1.0 (14 H, 2-H, 8-H, H's on cyclooctane ring, overlapping m's). **10** δ_H 5.13 (4-H, br, s), 2.87 (5-H, overlapping dd, $J_{1.5}$, $J_{5.6}$ 6.5), 2.43 (1-H, m, $J_{1.2}$, $J_{1.8}$ 6.5), 1.09 (6 H, d, CH_3) snd 2.00–1.20 (16 H, 2-H, 8-H, 2-propyl-H, H's on cyclooctane ring, overlapping m's).

(d) tert-*Butylbenzene*–(Z)-*cyclooctene.* The two major 1:1 adducts (ratio 1:1.5; *m*/*z* 244 (M^+); 2.5 g from irradiation of 100 cm^3 of an equimolar mixture of the addends for 36 h) were separated by preparative GC. **11** δ_H 5.76 (3-H, dd, $J_{3.4}$ 5.5, $J_{2.3}$ 2.0), 5.62 (4-H, dd, $J_{4.5}$ 2.5), 2.93 (5-H, m, $J_{5.6}$ 6.5), 2.41 (2 H, 6-H, 7-H, m), 1.94 (8-H, m, $J_{2.8}$ 6.0), 0.89 (9 H, s, CH_3) and 1.8–1.2 (13 H, 2-H, H's on cyclooctane ring, overlapping m's); δ_C (22.5 MHz), 133.57 (d), 132.22 (d), 57.76 (d), 56.79 (d), 45.17 (d), 40.88 (d), 27.16 (q), 32.81, 32.04, 31.05, 29.89, 29.50, 29.29, 26.48, 25.37 and 24.78 (overlapping signals), **12**: δ_H 5.15 (br.s), 2.96 (5-H, m, $J_{1.5}$ 6.5, $J_{4.5}$ 2.0, $J_{5.6}$ 6.0, $J_{5.7}$ 1.5), 2.50 (3 H, 1-H, 6-H, 7-H, overlapping m's), 1.12 (9 H, s, CH_3) and 2.0–1.0 (14 H, 2-H, 8-H, H's on cyclooctane ring, overlapping m's); δ_C(22.5 MHz), 154.89 (s), 122.17 (d), 56.24 (d), 55.91 (d), 44.84 (d), 38.90 (d), 36.70 (d), 29.48 (q), 33.00, 31.42, 30.37, 29.98, 27.89, 26.47, 25.31 and 24.72 (overlapping signals). The acidolysis of **12** into the alcohol[12] is described in ref. 16. *p*-Bromophenyl isocyanate (0.47 g) was added to the alcohol (0.62 g) in pentane. The mixture was refluxed for 30 h and cooled. The crystals of the *p*-bromophenyl urethane were filtered off and recrystallised from ethyl acetate (0.65 g, m.p. 166–167 °C). The X-ray crystallographic analysis of this urethane is described in ref. 12; δ_H([$^2H_5$]pyridine) 10.48 (1 H, s), 7.71 (2 H, d), 7.46 (2 H, d), 5.64 (1 H, s + fine splittings), 4.76 (1 H, overlapping dd), 3.16 (1 H, m), 2.86 (1 H, m), 2.5–2.0 (4 H, overlapping m's), 1.03 (9 H, s, CH_3), and 1.8–1.2 (12 H, overlapping m's). (Found: C, 65.5; H, 7.51; N, 3.07%. $C_{25}H_{34}O_2NBr$ requires C, 65.22; H, 7.39; N, 3.03%).

(e) *Bichromophoric arene–alkene systems.* The bichromophores **14a**, **b** and **15a**, **b** were synthesised by the methods described in ref. 20. The data from which the structural assignments of the photoproducts from **14b** and **15a**, **b** were deduced are also given in ref. 21. Separation of the three photoisomers from **14a** was achieved by flash chromatography and preparative GLC. **16**: *m*/*z* 186 (M^+); δ_H 5.84 (3-H, dd, $J_{2.3}$ 2.2, $J_{3.4}$ 6.0), 5.67 (4-H, dd, $J_{4.5}$ 2.0), 2.88 (5-H, m), 2.70 (2-H, dd, $J_{2.8}$ 6.5), 2.39 (7-H, m, $J_{7.8}$ 6.5) and 2.0–1.2 (13 H, 8-H, H's on propane bridges, overlapping m's). **17**: *m*/*z* 186 (M^+); δ_H 5.75 (3-H, dd, $J_{2.3}$ 2.5, $J_{3.4}$ 5.5), 5.58 (4-H, dd, $J_{4.5}$ 2.5), 3.00 (5-H, m, $J_{1.5}$ 5.2, $J_{5.6}$ 5.0), 2.58 (1-H, dd, $J_{1.2}$ 6.5), 2.29 (2-H, dd) and 1.95–1.2 (13 H, 6-H, H's on propane bridges, overlapping m's). **18**: *m*/*z* 186 (M^+); δ_H 5.63 (3-H, dd, $J_{2.3}$ 2.0, $J_{3.4}$ 5.0), 5.40 (4-H, d), 2.48 (1-H, dd), 2.15 (2-H, m), 2.05 (7-H, m, $J_{7.8}$ 6.5) and 1.9–1.2 (13 H, 8-H, H's on propane bridges, overlapping m's).

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References

1 K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, 1966, **88**, 2066.

2 D. Bryce-Smith, A. Gilbert and B. H. Orger, *J. Chem Soc.. Chem. Commun.*, 1966, 512.

3 P. A. Wender, L. Siggel and J. M. Nuss, *Organic Photochemistry*, ed. A. Padwa, Marcel Dekker, 1989, vol. 10, 357.

4 (*a*) E. M. Osselton, E. S. Krijnen, E. L. M. Lempers and J. Cornelisse, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 375; (*b*) D. Bryce-Smith, A. Gilbert and J. Mattay, *Tetrahedron*, 1986, **42**, 6011; (*c*) D. Bryce-Smith, *J. Chem. Soc., Chem. Commun.*, 1969, 806.

5 P. de Vaal, E. M. Osselton, E. S. Krijnen, G. Lodder and J. Cornelisse, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 407; and references therein.

6 A. Gilbert, P. Heath and P. W. Rodwell, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1867.

7 H. Leismann, J. Mattay and H-D. Scharf, *J. Am. Chem. Soc.*, 1984, **106**, 3985.

8 E. M. Osselton, J. J. van Dijk-Knepper and J. Cornelisse, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1021.

9 J. A. van der Hart, J. J. C. Mulder and J. Cornelisse, *J. Mol. Struct.*, 1987, **151**, 1.

10 H-D. Scharf and J. Mattay, *Tetrahedron Lett*, 1977, **18**, 401; J. Mattay, H. Leismann and H-D. Scharf, *Chem. Ber.*, 1979, **112**, 557; J.

Mattay, J. Runsink, J. A. Piccirilli, A. W. H. Jans and J. Cornelisse, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2333; E. M. Osselton, J. Cornelisse and J. Mattay, *J. Photochem.*, 1985, **31**, 381; J. Mattay, J. Runsink, R. Hertel, J. Kalbe and I. Schewe, *J. Photochem.*, 1987, **37**, 335.

11 A. Gilbert and P. Heath, *Tetrahedron Lett.*, 1979, **20**, 2831; D. Bryce-Smith, G. A. Fenton and A. Gilbert, *Tetrahedron Lett.*, 1982, **23**, 2697.

12 D. Bryce-Smith, M. G. B. Drew, G. A. Fenton and A. Gilbert, *J. Chem. Soc., Chem. Commun.*, 1985, 607.

13 See also K. N. Houk, *Pure Appl. Chem.*, 1982, **54**, 1633.

14 E. M. Osselton, Ph.D. Thesis, Leiden University, The Netherlands, 1987.

15 D. Bryce-Smith, B. E. Foulger, J. Forrester, A. Gilbert, B. H. Orger and H. M. Tyrrell, *J. Chem. Soc., Perkin Trans. 1*, 1980, 55.

16 G. A. Fenton and A. Gilbert, *Tetrahedron*, 1989, **45**, 2979.

17 See for example A. W. H. Jans, J. Lugtenburg, J. Cornelisse and C. Kruk, *Org. Magn. Reson.*, 1982, **19**, 58.

18 J. C. Berridge, J. Forrester, B. E. Foulger and A. Gilbert, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2425.

19 V. Y. Merritt, J. Cornelisse and R. Srinivasan, *J. Am. Chem. Soc.*, 1973, **95**, 8250.

20 R. B. Cundall and D. A. Robinson, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1691.

21 G. C. R. Ellis-Davies, A. Gilbert, P. Heath, J. C. Lane, J. V. Warrington and D. L. Westover, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1833.

22 A. Gilbert and G. N. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1761.

23 R. S. Sheridan, *Tetrahedron Lett.*, 1982, **23**, 267.

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