

SELECTIVITIES IN PHOTOCYCLOADDITIONS OF ARENES TO OLEFINS

JOCHEN MATTAY

Institut für Organische Chemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, D-5100 Aachen (F.R.G.)

(Received July 7, 1986; in revised form August 20, 1986)

Summary

The regioselectivities and stereoselectivities of photoreactions of arenes to olefins are discussed on the basis of the exciplex mechanism. As shown earlier for the mode of reaction, these selectivities are also influenced by the photoinduced charge transfer. In addition to the exciplex, dipolar intermediates are considered in order to explain the high regioselectivities of photocycloadditions with donor- and acceptor-substituted arenes.

1. General remarks

The photoreactions of olefins to arenes have been investigated for a long time [1] starting from the early discoveries of the ortho [2 - 5] and the meta cycloadditions [6, 7] (Fig. 1). Different mechanisms have been proposed, especially for the meta cycloaddition [8], but only the one involving an excited state intermediate (exciplex) provides a rationalization which is sufficiently in accord with the experimental evidence (eqn. (1)):



where Ar denotes arene and Ol denotes olefin.

Intermediates of this type have been proposed earlier by Ferree *et al.* [9] and by Srinivasan and Ors [10]. Their existence and their role as reactive intermediates were proven later in this laboratory [11, 12]. Meanwhile, numerous investigations supporting this mechanism have been reported by various groups [13 - 24] and just recently we have presented an empirical correlation between the free enthalpies of electron transfer and the modes of reaction (substitution, ortho and meta cycloaddition) of arene-olefin systems [23, 24] (Fig. 1). This rationalization is based on the exciplex mechanism and the Weller equation [25]. A simplified version is given as follows:

$$\Delta G = F[E_{1/2}^{\text{ox}}(\text{D}) - E_{1/2}^{\text{red}}(\text{A})] - \Delta E_{\text{excit}} + \Delta E_{\text{coul}} \quad (2)$$

where F is the Faraday constant, $E_{1/2}^{\text{ox}}(\text{D})$ is the oxidation potential of the donor, $E_{1/2}^{\text{red}}$ is the reduction potential of the acceptor, both in acetonitrile (simply measurable, *e.g.* by means of cyclic voltammetry), ΔE_{excit} is the

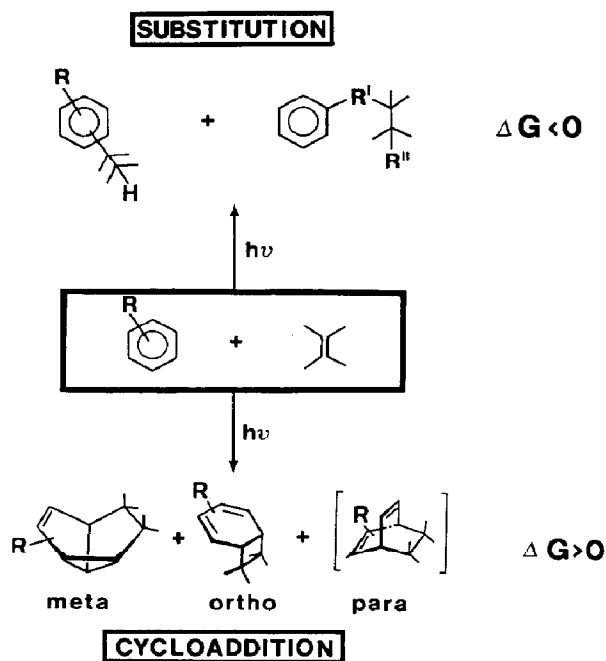


Fig. 1. Mode of reaction and photoinduced electron transfer.

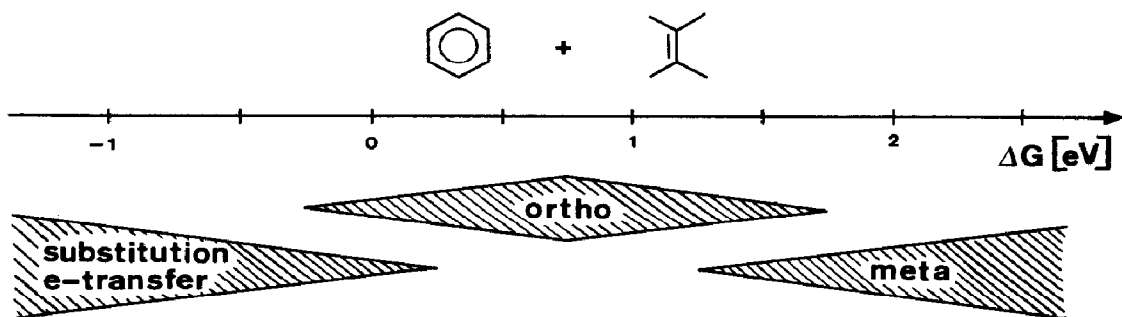


Fig. 2. Correlation of modes of reactions (substitution, ortho and meta cycloadditions) with free enthalpies of electron transfer (for more detailed versions, see refs. 23 and 24).

excitation energy of the electronically excited species, and ΔE_{coul} is the coulombic interaction energy in a given solvent. ΔE_{coul} is derived from the Born equation as shown by Weller [25] and is easy to calculate using the dielectric constant ϵ of the solvent (for applications of eqn. (2) see, for example, refs. 22 - 24).

This rationalization not only refers to the ortho cycloaddition–meta cycloaddition relationship [24] and therefore appears to be an extension of the ΔIP (ionization potential) correlation of Bryce-Smith and coworkers [26, 27], but it also includes the substitution reactions between photo-excited arenes and olefins [23] (Fig. 2). Moreover, even stereochemical effects of cycloadditions appear somewhat clearer [22 - 24, 28 - 31]. The reason that in a given series most examples fit the ΔG correlation may be

attributed to the fact that here the charge transfer within excited state intermediates is considered and, furthermore, the direction of charge transfer (CT) in the exciplex state can now be determined [23, 24]. This means that, besides a qualitative categorization into exciplexes of weak or strong charge transfer character which corresponds to the influence of the CT state of the exciplex according to eqn. (3) [32 - 34], we can also find out which of the reactants, the arene or the olefin, acts as acceptor or donor (see formula A of Fig. 3).



where A is an electron acceptor and D is an electron donor.

In addition to the exciplex A, dipolar intermediates B and C have been proposed in order to explain the high regioselectivities of meta and ortho photocycloadditions with donor and acceptor substituted benzenes [14, 17, 18, 20, 22, 27 - 31, 35 - 39]. (It should be noted that these singlet species are not necessarily electronically symmetrical, especially when strong perturbing groups are present.)

Both the exciplex and the dipolar intermediate are formed consecutively from the starting compounds on irradiation. Whereas the first step, *i.e.* the quenching of the excited singlet state of the arene under formation of an exciplex A is an adiabatic process [12, 40], the second intermediate with either two newly formed σ -bonds (B) (leading to meta cycloadducts) or with one σ -bond (C) (leading to ortho cycloadducts) is already at a minimum on the energy surface of the ground state of the product [16, 41]. From these considerations, the formation of B or C is a diabatic photoreaction. Although the exact shapes of the energy surfaces, including their minima, are not yet known from spectroscopic results or even from calculations [42], investigations on the stereochemistry of photoadditions of 2-methyl-1,3-dioxole to benzene and to anisole [28], and on deuterium isotope effects in the corresponding cycloadditions of toluene and anisole to cyclopentene [42] indicate, at least for the meta cycloaddition, some polarization within the arene moiety even before the two new σ -bonds of B are completely formed (Fig. 4).

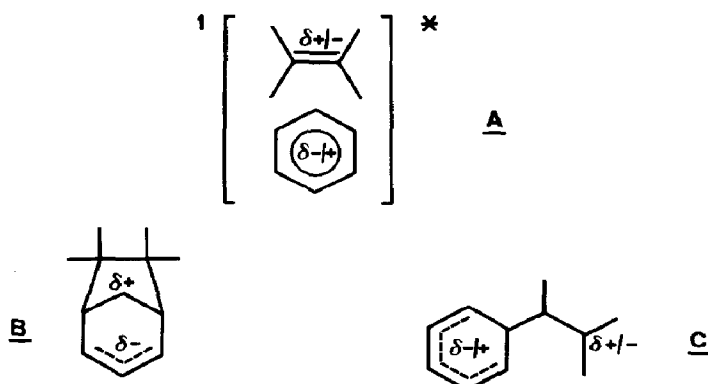


Fig. 3. Charge separation on polar intermediates.

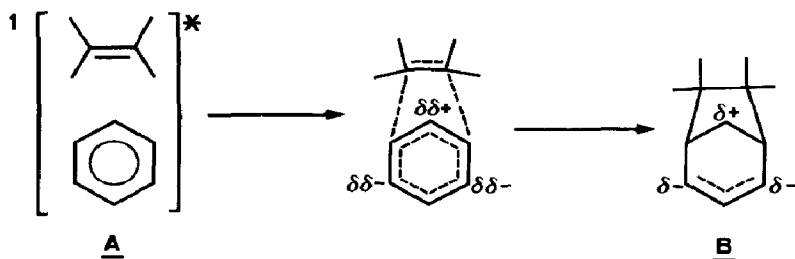


Fig. 4. Polarization of the arene in the process A \rightarrow B.

Moreover, the CT character of the exciplex seems to influence the charge separation within the arene part of the medium structure (Fig. 4) or even of B itself as shown for the photoreactions of α,α,α -trifluorotoluene with olefins [22]. There is no doubt that similar polarizations are effective in the ortho cycloaddition process.

The mode selectivities of photoreactions between arenes and olefins have already been discussed in detail elsewhere [23, 24] and therefore will not be presented here (Fig. 2). Only one point need be stressed: correlations between free enthalpies of electron transfer and the mode of the reactions (selectivities) are empirical and therefore may be restricted to one series of molecules owing to similar structural features of the intermediates, *i.e.* absolute values of ΔG may change in some series. However, we could show the more general character of these correlations, at least for the photoreactions of arenes with olefins (*e.g.* see photoreactions of benzene and of benzonitrile) [23, 24].

Cycloaddition products of the para type are only formed in some special examples such as in Yang's "allowed" $4\pi_s + 4\pi_s$ cycloadditions of benzenoid aromatic hydrocarbons to dienes [43, 44], in additions of benzene to furans [45, 46], and in reactions with allenes [47] and with fluoroarenes [48]. Simple olefins occasionally form para cycloadducts with benzene and its substituted derivatives but our investigations of reactions with 1,3-dioxoles [11] and dichlorovinylene carbonate [49] clearly revealed that this mode of cycloaddition occurs from the secondary photochemical event. Therefore the following discussion of the regioselectivities and stereoselectivities of cycloadditions of olefins to arenes is only concerned with the primary meta and ortho modes. We will summarize the features of these cycloadditions in terms of the exciplex "zwitterion" mechanism. (We have occasionally termed the polar intermediates which are involved in photocycloadditions of arenes to olefins as "zwitterions" (see, for example, refs. 22, 29 - 31) always considering that the dipolar character depends on the substitution and the charge transfer of the exciplex.) The need for such a rationalization dealing mainly with donor- and acceptor-substituted arenes arises not only from mechanistic reasoning but also from recent successes in sophisticated organic syntheses of natural [50] and other important products [51].

2. Regioselectivity

Most of the studies of the regioselectivity in cycloadditions of substituted benzenes deal with the meta cycloaddition. We shall therefore discuss this topic in more detail before considering aspects of the ortho cycloadditions.

2.1. Meta cycloadditions

Recent studies of meta cycloadditions of olefins to substituted benzenes have been reported for anisole and its derivatives [10, 15, 18, 37 - 39, 52 - 58], toluene and its derivatives [13, 15, 20, 21, 37, 59 - 61], benzonitrile [39, 53, 55 - 57, 61 - 63], methyl benzoate [54, 62], trifluorotoluene [19, 22, 61, 63] and fluorobenzene [20, 52, 61, 64]. For earlier reports see refs. 1, 8 and 41.

On inspection of all the meta cycloadditions of olefins to these substituted benzenes, the following trends can be observed.

(1) Donor (D) substituents are always placed in position 1 of the meta adduct; in particular, alkoxy has priority over alkyl.

(2) Acceptor (A) substituents are generally located in position 2 or 4 of the product.

The origin of these features can be understood on the basis of a dipolar intermediate (4 in Fig. 5). The assumption of such an intermediate is in accordance with the exciplex mechanism, since we could show from our kinetic studies that an exciplex 3 is a necessary but not a direct precursor of the products [12].

Although "zwitterions" of this type have not been directly observed, the following results imply their existence.

(1) A biradical which is structured in the same way as the "zwitterion" cannot account for the regioselectivities observed with donor-substituted benzenes, *e.g.* methylanisoles should yield mixtures of 1-methoxy- and 1-methyl-regioisomers (for radical stabilization, see for example Viehe *et al.* [65]). However, in species of cationic character (carboxonium ion) methoxy has a stronger stabilizing effect.

(2) Analogous arguments hold for acceptor-substituted benzenes.

(3) Studies of the influence of solvent polarity on product formation suggest the involvement of polar intermediates [22, 53, 58].

(4) Last but not least, the mechanism via a prefulvene intermediate cannot rationalize the selectivities at all, as shown recently by Sheridan [15]. The same holds for a concerted mechanism.

An intermediate of the prefulvene type resulting from σ -bond formation in the excited arene as the initial step has been proposed in an early report [6] and has been discussed on various occasions later [8, 41]. However, see also refs. 13 and 27. Meanwhile, further research necessitated the alternative exciplex mechanism (see below).

A fully concerted process between S_1 benzene and S_0 alkene, *i.e.* one in which all three bonds of the meta adduct are formed synchronously, has

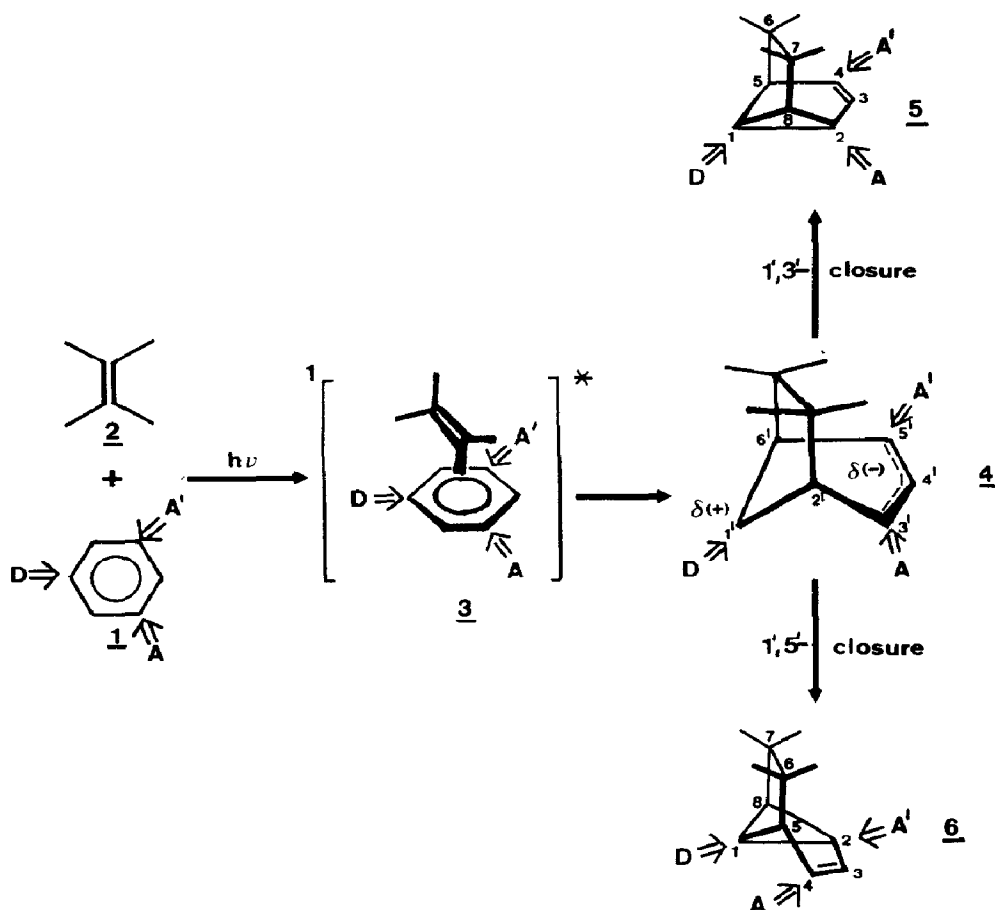


Fig. 5. Regioselectivity in meta photocycloadditions of olefins to substituted benzenes: A, electron-acceptor substituent; D, electron-donor substituent. All structures discussed are racemic.

been proposed on the basis of an orbital symmetry analysis [41, 66, 67]. However, such a mechanism has been shown to be unlikely both from experimental results [13, 37] and from theoretical considerations [16].

Some examples may clarify these arguments (for references see Fig. 6).

All the olefins which have been employed so far yield 1-substituted meta adducts with anisole (7 - 10, 12 - 15). The photoreactions with phenyl trimethylsilyl ether result in similar products (20 - 22). Compound 11 is the only product of the photoreaction of 3,5-dimethylanisole with cyclopentene. Alkyl benzenes also form 1-alkylsubstituted meta adducts (16 - 18); further substitution by fluorine does not alter the regiochemistry (19). The same holds for photoreactions with 3-fluoroanisole (27, 28) and 3-methoxybenzonitrile (34, 35); the meta adducts 23 - 26 (from α,α,α -trifluorotoluene and cyclopentene or 1,3-dioxole) demonstrate the influence of acceptor substituents. Analogous regioselectivities have been observed in the photoreactions of benzonitrile with olefins (29 - 33).

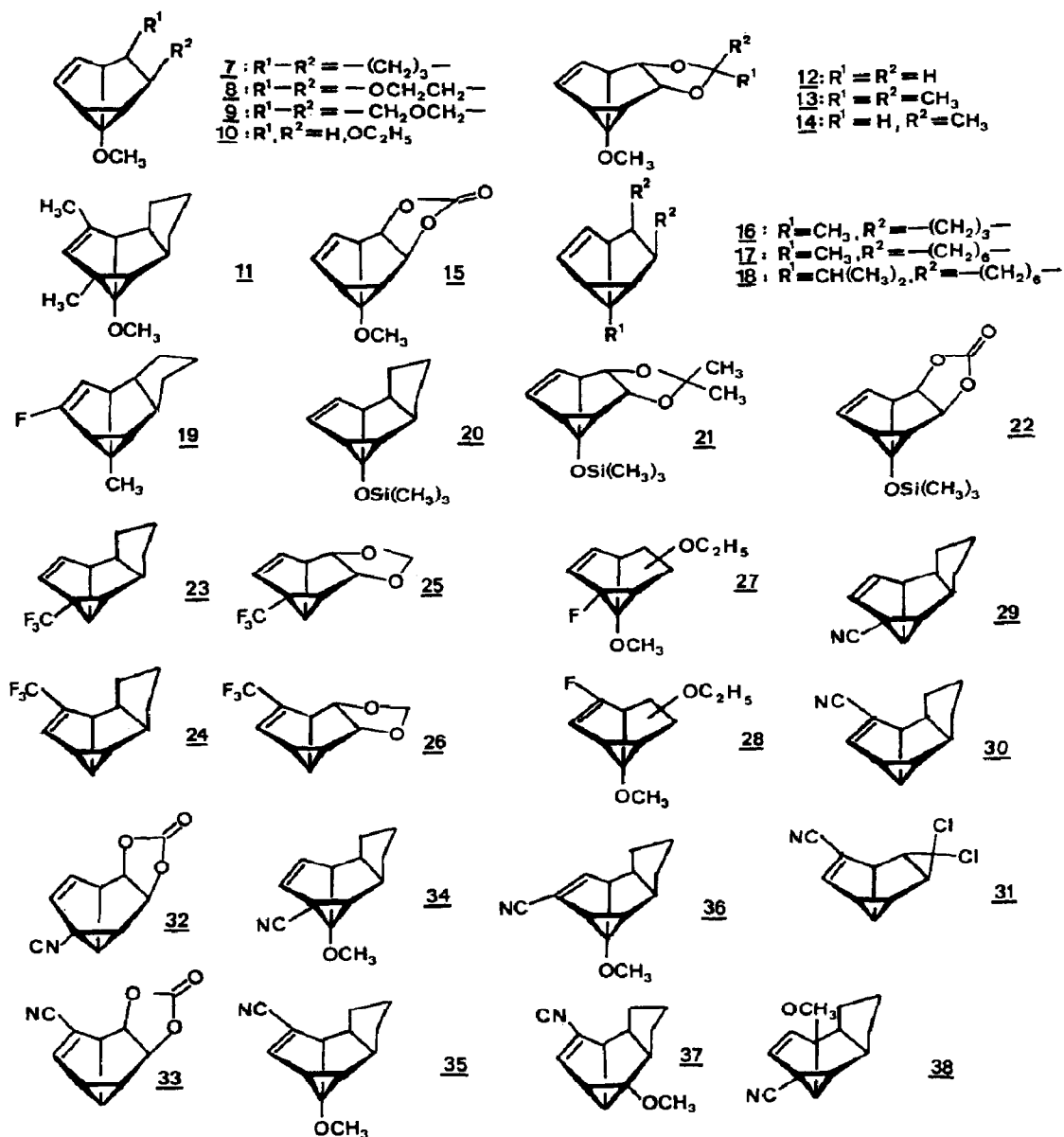


Fig. 6. Main products of meta cycloadditions of olefins to donor- and acceptor-substituted benzenes. Regioselectivities are determined by the donor substituents (7 - 22), the acceptor substituents (23 - 26, 29 - 33) or both (27, 28, 34 - 38). Competing effects are observed in 19, 36 - 38.

<i>Product</i>	7 - 10	11	12, 13	14	15	16	17, 18	19	20 - 22	23, 24	25, 26	27, 28	29, 30	31	32, 33	34 - 38
<i>Reference</i>	18	68	29	28	55, 69, 31	21	20	31	63	22	70	63	61, 55, 62	56, 58		

The electronic stabilizations of both donor and acceptor substituents do complement one another in the meta benzenes (*e.g.* see products **27**, **28**, **34**, **35**). However, as shown by Cornelisse, only one type of substituent operates in photoreactions of the corresponding para isomers. Three regioisomeric meta adducts are formed with 4-methoxybenzonitrile and cyclopentene in a ratio of [36]:[37]:[38] = 45:20:15 [56, 58]. Either methoxy is placed in position 1 (and consequently cyano in position 3 in **36**) or cyano is placed in position 4 or 2 (and consequently methoxy in position 8 in **26** or 5 in **38**). The 4-cyano-8-methoxy meta adduct should also be formed according to the above-mentioned rules, and indeed it has recently been detected [58].

The degree and the direction of charge transfer in the exciplex intermediate may also influence the regioselectivity as we have shown for the photocycloaddition of vinylene carbonate to α,α,α -trifluorotoluene [22]: here four regioisomeric meta adducts are formed with a small preference for the 2- and 4-substituted products as expected from the above-mentioned rules. The charge separation is relatively weak and, moreover, it is reversed compared with the photoreactions with alkenes and donor olefins as can be simply deduced from Weller's theory of electron transfer [22 - 24]. In this case, CF_3 as the stabilizing acceptor substituent does not have the same strong influence as, for example, in corresponding systems with 1,3-dioxole or cyclopentene [22, 63] which show stronger charge separations [22 - 24]. This means that by the time the orientation is determined (see **3** in Fig. 5), the dipolar character of the six-membered ring (see **4** in Fig. 5) is already developed. As a consequence the charge separation in the exciplex **3** influences the dipolar character of the intermediate **4** in a proportional manner (see Fig. 4). For a more detailed discussion of the photoreactions with trifluorotoluene see ref. 22. It should be specifically noted that the stereoselectivity of meta cycloadditions is also influenced by similar effects [28] (see below).

Starting from the above discussion, we may consider intermediates of the structure **4** in arene-olefin systems which exhibit extremely weak CT character as biradicals rather than "zwitterions". For example, the charge separation in alkyl benzene-alkene systems is very small according to $\Delta G > 2$ eV of electron transfer, which can be estimated from the Weller equation [23, 24]. (Exact values of ΔG cannot be calculated since the reduction potentials of alkyl benzenes are not measurable. The current limit has been reached with benzene (see ref. 23).) Therefore, the meta-bonded intermediates involved in photoreactions of xylenes and cyclopentene have biradical rather than zwitterionic character. This rationalization corresponds to the results of Sheridan on the "independent generation of arene meta photoaddition biradicals" [71].

2.2. Ortho cycloadditions

Despite the generally lower regioselectivities of the ortho cycloadditions in comparison with the meta mode the following trend is observed. The selectivities between 1,2-, 2,3- and 3,4-attack of the olefin on the arene

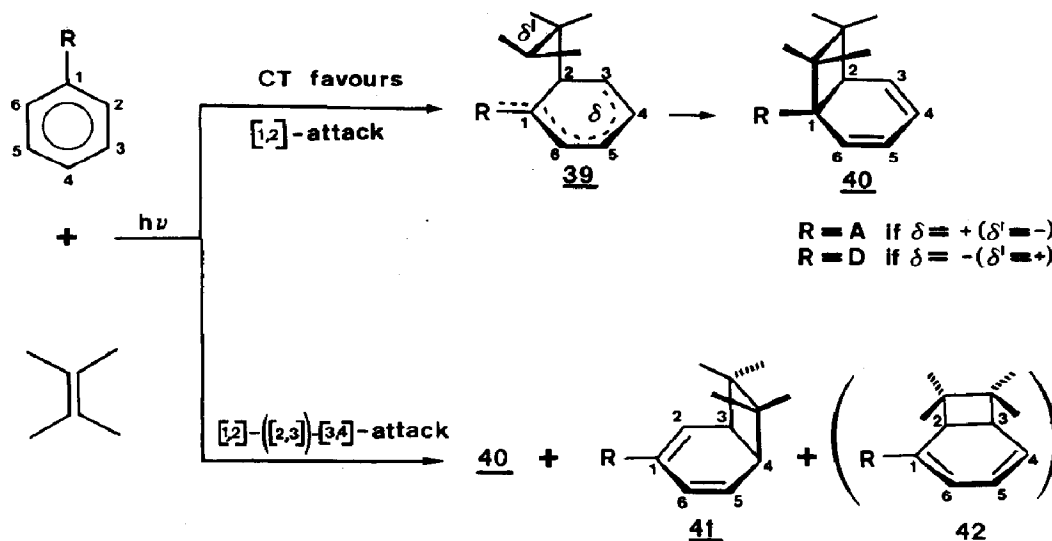


Fig. 7. Regioisomeric ortho cycloadducts from monosubstituted benzenes and olefins: δ , partly charged dipolar intermediates of the type 39 (signs depend on the direction of the charge transfer (see text)); A, acceptor substituent; D, donor substituent.

depend on the CT character of the intermediates, *i.e.* the regioselectivity is high (low) if ΔG of electron transfer is relatively low (high) (see refs. 23 and 24 for application of the Weller equation). Figure 7 demonstrates that in the former case, 1-substituted ortho adducts 40 are preferentially formed (especially if a substituent R in 39 stabilizes charges $\delta(\pm)$ in position 1), whereas in the latter case, mixtures of regioisomers 40 and 41 are obtained.

The formation of 40 may be rationalized analogously to that of the meta adducts 5 or 6 simply by assuming stepwise bond formation as shown in the case of the photoaddition of 1,3-dioxole to anisole [29] (Fig. 8). Here an exciplex with a polarization as shown in 43 [23, 24, 29] may be the precursor of the meta adduct 12 and the ortho adduct 45. The methoxy

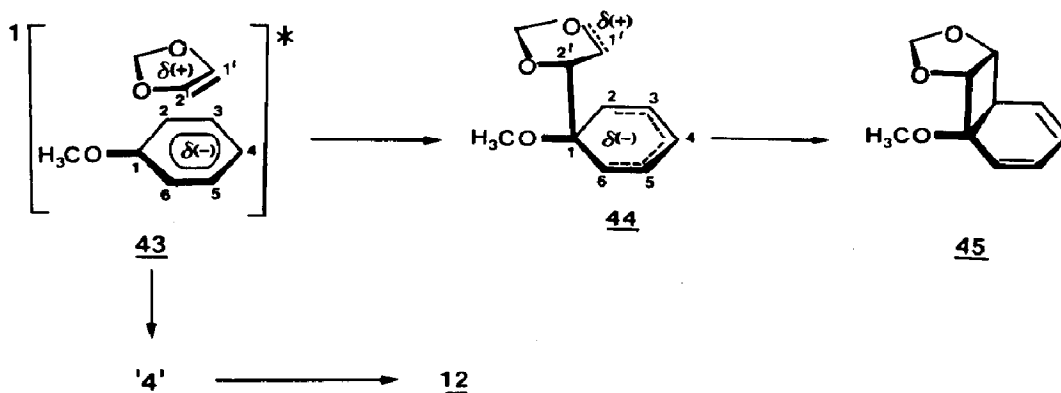


Fig. 8. Stepwise formation of the exo ortho adduct from anisole and 1,3-dioxole via polar intermediates.

substituent is located at position 1 of the intermediate. The rotation around the C1—C2' bond in **44** plays a minor role since the endo isomer is formed in only small amounts. These effects have been discussed in detail elsewhere [29].

A series of benzonitrile-olefin systems was investigated by Cantrell [72] and the results support our considerations. Further examples are presented in Fig. 9. Toluene and anisole preferentially form **47** on reaction with acrylonitrile [38, 60, 73]. The formation of **51** and **52** from trifluorotoluene and 1,3-dioxole may best be rationalized by assuming dipolar intermediates (**49** and **50** respectively [22]). The same arguments account for **53** [53]. All these systems have in common that ΔG generally does not range above about 0.5 eV, indicating a relatively high degree of charge transfer in the exciplex intermediate [22]. This is in accordance with increasing regioselectivity of the ortho cycloaddition in highly polar solvents [38, 58, 60].

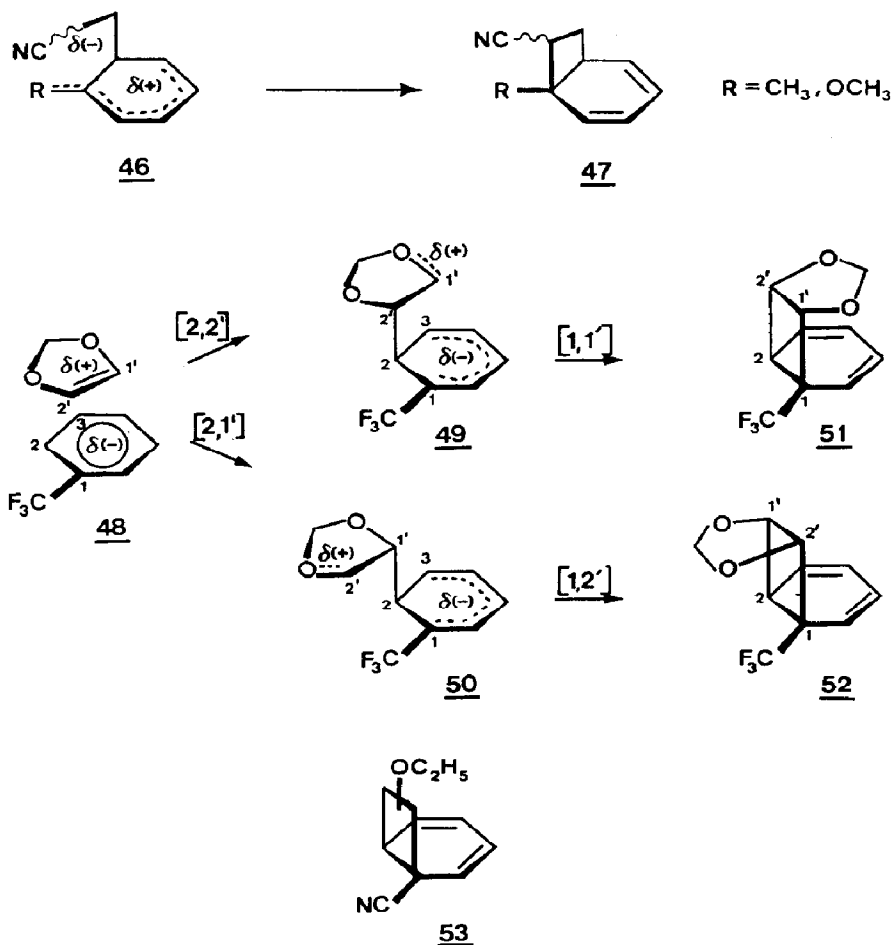


Fig. 9. Regioselectivity and stereoselectivity in ortho cycloaddition of olefins to substituted benzenes.

It should be noted that dipolar intermediates of type **39** have already been discussed earlier, *e.g.* in the photoaddition of maleic anhydride to benzene which has been extensively studied by Bryce-Smith, Gilbert and coworkers [8, 17, 41, 74]. Only a few ortho cycloadditions have been reported which exhibit high ΔG values near the transition area between the ortho and the meta modes [23, 24]. These known examples clearly support the second part of our proposal shown in Fig. 7, *e.g.* benzonitrile and acrylonitriles or methyl acrylates yield mixtures of regioisomers on photolysis [75]. More systematic studies have to be done before any explanation can be given about the fact that the regioisomer **42** has not yet been found in these systems [60, 75].

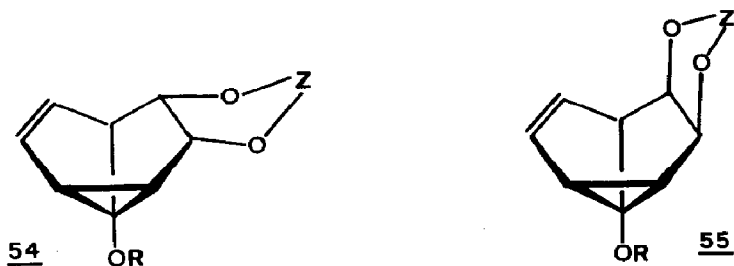
3. Stereoselectivity

Most of the studies of the stereoselectivity (endo:exo ratio) in photo-reactions of arenes deal with the meta cycloadditions, since in these the selectivities are more clearly defined. This may be due to the limited degrees of freedom in intermediates which are involved in this type of cycloaddition.

3.1. Meta cycloadditions

The endo stereoselectivity observed in most meta cycloadditions has been rationalized by Houk [16] on the basis of secondary orbital interactions in the exciplex state. However, these selectivities are only observed in systems of extremely weak CT character such as benzene-alkenes. Turning to enol ethers, the stereoselectivity is weakened, *e.g.* ethyl vinyl ether adds to benzene only 60% stereoselectively towards the endo isomers [60] and the endo:exo ratio of meta adducts from anisole and 2,3-dihydrofuran or ethyl vinyl ether are nearly unity [18]. Moreover, the selectivity is reversed in cycloadditions of enediol ethers to arenes [14, 22, 28, 29, 31]. One example which has been investigated more recently [29] is shown in Fig. 8. These striking effects may be due to a destabilization of the endo configuration by the repulsion between the oxygen atoms and the partly negatively charged arene favouring **43** and "4" (Fig. 8). This destabilization is also reflected in the anomalous high repulsion energy, $E_{\text{rep}} = 147 \text{ kJ mol}^{-1}$, which we have determined for the benzene-trimethyl-1,3-dioxole system, compared with that of 59 kJ mol^{-1} for the "normal" benzene-triethylamine exciplex system [76]. Analogous naphthalene systems show similar results [77]. Again, the direction of charge transfer has to be considered: vinylene carbonate as an acceptor olefin induces a reversed charge transfer resulting in a partly positively charged arene which will then stabilize the endo configuration. Indeed, this olefin preferentially adds endo to benzene [78], trifluorotoluene [22], anisole [31, 55], and trimethylsiloxybenzene [31].

Some special features may be emphasized. The stereoselectivity of meta cycloadditions of cyclic enediol ethers and esters to anisole and trimethylsiloxybenzene changes in favour of the exo isomer with the silyl ether



R	Z	55 : 54
CH ₃		1 : 3.2
	C(CH ₃) ₂	
Si(CH ₃) ₃		1 : 9.3
CH ₃		2.0 : 1
	C=O	
Si(CH ₃) ₃		1.3 : 1

Fig. 10. Stereoselectivities in meta cycloadditions of anisole and trimethylsilyl phenyl ether to 1,3-dioxole derivatives.

despite more steric hindrance [31] (Fig. 10). This finding indicates secondary bonding interactions in polar intermediates which even overcome geometric restrictions due to the capability of silicon to expand its coordination by $p \rightarrow d$ bonding.

However, under certain molecular conditions the stereoselectivity may be altered as shown for meta cycloadditions of *m*-bis(trifluoromethyl)-benzene to cyclopentene [30] (Fig. 11).

This reversal of the "normal" endo stereoselectivity in favour of the exo mode is only observed when both CF₃ groups are located in positions 1'

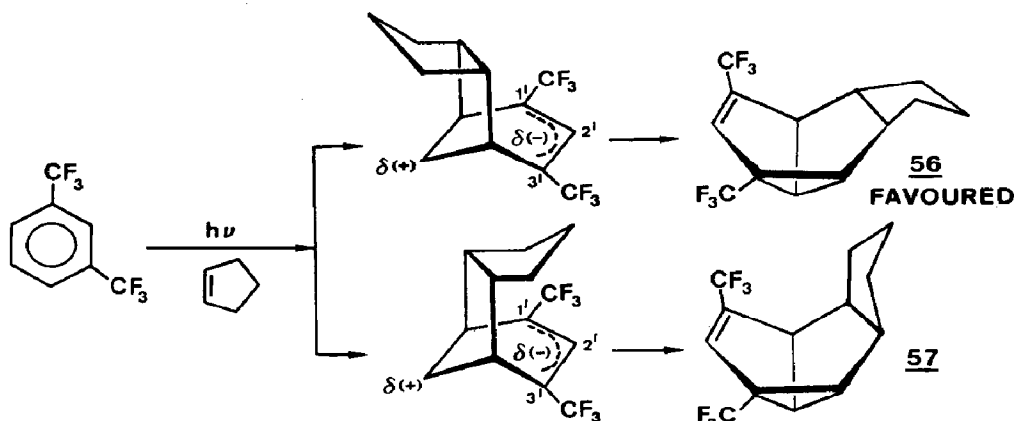


Fig. 11. Steric hindrance during the endo meta cycloaddition of *m*-bis(trifluoromethyl)-benzene to cyclopentene.

and 3' of the arene, which corresponds to a 4',6'-attack of the olefin onto the arene (see Fig. 11). Steric hindrance now overcomes the secondary bonding interactions which normally determine the endo stereoselectivity [16, 30]. It should be noted that contrary to the stereoselectivity the regioselectivity remains unaffected. (CF_3 as acceptor substituent is located in position 2 and 4 of the meta cycloadduct as expected from the above-mentioned rules.) The corresponding cycloaddition with cyclohexene yields similar results [30]. Bryce-Smith *et al.* have reported on the meta cycloadditions of alkenes to alkylbenzenes [21]. They found that, contrary to the above-mentioned systems, the regioselectivity changes progressively from 2,6- to 3,5-attack with increasing size of the alkyl groups while retaining endo stereoselectivity. The researchers have rationalized this finding in terms of a weak but orienting intermolecular bonding interaction between S_1 benzene and the α -hydrogens on the alkene which can predominate over steric effects of bulky alkyl groups. This "intermolecular hyperconjugation" is somewhat similar to Houk's secondary bonding interaction [16].

3.2. Ortho cycloadditions

Here the stereoselectivities are similarly determined as discussed previously for the meta cycloadditions. In particular, this holds for photoreactions of benzene and its donor-substituted derivatives, *e.g.* both the meta and the ortho adducts from the additions of 1,3-dioxoles to benzene and anisole respectively, exhibit the exo configuration as outlined in Fig. 6 [14, 18, 28, 29]; alkenes such as *cis*-cyclo-octene and 2-butene add predominantly endo to benzene in both reaction modes [8]. However, the differentiation between endo- and exo-attack is smaller for acceptor-substituted benzenes and acceptor olefins: *e.g.* despite their pronounced CT character, trifluorotoluene-1,3-dioxole systems show no preference for any stereoisomer in the ortho-cycloaddition mode [22]; further examples are the photoreactions of benzene with acrylates and methyl vinyl ketone [8]. These examples demonstrate that various aspects have to be considered in rationalizing the stereoselectivities in ortho cycloadditions such as the CT character of the starting molecules, the stabilization effects of substituents, and last but not least, the solvent polarity [79]. Furthermore, in some special cases ground-state complexes may determine the stereochemistry as in the benzene maleic anhydride system, which exclusively forms products in the exo configuration [8, 17, 41, 74]. Cycloadditions via electronically excited olefins may not necessarily be understood on the basis of this rationalization, *e.g.* both maleimide [17] and thiochromone-1,1-dioxide [80] form exo ortho adducts via S_1 (olefin).

Conclusions

In summary, the selectivities of the photoreactions of benzene and its substituted derivatives with olefins can be rationalized on the basis of the

exciplex mechanism. Charge transfer within the exciplex intermediates strongly influences not only the modes of reaction but also the regioselectivities and stereoselectivities. An empirical correlation between these selectivities and the charge transfer, which can be estimated by means of the Rehm-Weller equation, has been presented [23, 24]. According to this equation the free enthalpy ΔG of electron transfer can be easily calculated from the redox potentials of the starting molecules and from the excitation energy of the electronically excited species.

Besides the exciplex and its CT character, dipolar intermediates have to be considered in cycloaddition reactions of substituted benzenes:

(1) In meta cycloadditions donor (acceptor) substituents are generally located in position 1 (2 and 4) of the products, and this corresponds to a 2',6'- (2',4'-) attack of the olefin onto the arene.

(2) The regioselectivities of ortho cycloadditions are smaller owing to more degrees of freedom in their intermediates of type 34. However, the 1',2'-attack is preferred if ΔG is relatively small, *i.e.* if the CT character of the exciplex is high.

(3) Factors such as the extent and the direction of charge transfer and the charge stabilization by substituents also influence the stereoselectivity.

(a) Secondary orbital interactions determine the stereochemistry of the products at least for the meta mode, *e.g.* the "normal" endo selectivity is reversed in enediol ether systems owing to the repulsion between the oxygens and the partly negatively charged arene.

(b) The stereoselectivities, which are observed in ortho cycloadditions of benzene and its donor-substituted derivatives, are subject to conditions similar to those outlined for the meta mode. However, this does not account for the reactions of acceptor-substituted benzenes and olefins.

Here we have discussed only the selectivities of intermolecular photocycloadditions. If geometrical restrictions are not too strong, the intramolecular cycloadditions show similar regioselectivities as has been shown earlier by Ferree *et al.* [9] and later by Gilbert and Taylor [81] and Ellis-Davis and Cornelisse [20], and in elegant synthetic applications by Wender and Singh [50] and by Keese and coworkers [51, 82]. However, intramolecular restrictions caused by the geometry and the substitution of the bichromophoric compounds may alter the regiochemical and stereochemical course of these photocycloadditions [8, 9, 51, 81 - 84].

Acknowledgments

Financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged. The author is also very grateful to all coauthors of the joint papers.

References

- 1 A. Gilbert, in D. Bryce-Smith (ed.), *Photochemistry* (Specialist Periodical Reports), The Royal Society of Chemistry, London, Vol. 1 - 16.
- 2 D. E. Ayer and G. H. Buchi, *U.S. Patent*, 2,805,242, 1957; *Chem. Abstr.*, 52 (1958) 2904a.
- 3 H. J. F. Angus and D. Bryce-Smith, *Proc. Chem. Soc.*, (1959) 326; *J. Chem. Soc.*, (1960) 4791.
- 4 G. O. Schenck and R. Steinmetz, *Tetrahedron Lett.*, 1 (1960) 1.
- 5 E. Grovenstein, D. V. Rao and J. W. Taylor, *J. Am. Chem. Soc.*, 83 (1961) 1705.
- 6 D. Bryce-Smith, A. Gilbert and B. H. Orger, *Chem. Commun.*, (1966) 512.
- 7 K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, 88 (1966) 2066.
- 8 A. Gilbert, *Pure Appl. Chem.*, 52 (1980) 2669.
- 9 W. Ferree, G. B. Grutzner and H. Morrison, *J. Am. Chem. Soc.*, 93 (1971) 5502.
- 10 R. Srinivasan and J. A. Ors, *Chem. Phys. Lett.*, 42 (1976) 506 and earlier reports.
- 11 J. Mattay, H. Leismann and H.-D. Scharf, *Chem. Ber.*, 112 (1979) 577; *Mol. Photochem.*, 9 (1979) 119.
- 12 H. Leismann, J. Mattay and H.-D. Scharf, *J. Am. Chem. Soc.*, 106 (1984) 3985.
- 13 D. Bryce-Smith, G. A. Fenton and A. Gilbert, *Tetrahedron Lett.*, 23 (1982) 2697.
- 14 J. Mattay, J. Runsink, H. Leismann and H.-D. Scharf, *Tetrahedron Lett.*, 23 (1982) 4919.
- 15 R. S. Sheridan, *Tetrahedron Lett.*, 23 (1982) 267.
- 16 K. N. Houk, *Pure Appl. Chem.*, 54 (1982) 1633.
- 17 D. Bryce-Smith, A. Gilbert, N. Al-Jalal, R. R. Deshpande, J. Grzonka, M. A. Hems and P. Yianni, *Z. Naturforsch., Teil B*, 38 (1983) 1101.
- 18 A. W. H. Jans, B. van Arkel, J. J. van Dijk-Knepper, H. Mioch and J. Cornelisse, *Tetrahedron*, 40 (1984) 5071.
- 19 J. Mattay, J. Runsink, T. Rumbach, C. Ly and J. Gersdorf, *J. Am. Chem. Soc.*, 107 (1985) 2557.
- 20 G. C. R. Ellis-Davies and J. Cornelisse, *Tetrahedron Lett.*, (1985) 1893, and earlier reports.
- 21 D. Bryce-Smith, M. G. B. Drew, G. A. Fenton and A. Gilbert, *J. Chem. Soc., Chem. Commun.*, (1985) 607.
- 22 J. Mattay, J. Runsink, J. Gersdorf, T. Rumbach and C. Ly, *Helv. Chim. Acta*, 69 (1986) 442.
- 23 J. Mattay, *Tetrahedron*, 41 (1985) 2393.
- 24 J. Mattay, *Tetrahedron*, 41 (1985) 2405.
- 25 A. Weller, *Z. Phys. Chem., N.F.*, 133 (1982) 93.
- 26 D. Bryce-Smith, A. Gilbert, B. H. Orger and H. M. Tyrrell, *Chem. Commun.*, (1974) 334.
- 27 D. Bryce-Smith, A. Gilbert and J. Mattay, *Tetrahedron Lett.*, 21 (1986) 6011.
- 28 E. M. Osselton, J. Cornelisse and J. Mattay, *J. Photochem.*, 31 (1985) 381.
- 29 J. Mattay, J. Runsink, J. Piccirilli, A. W. H. Jans and J. Cornelisse, *J. Chem. Soc., Perkin Trans. I*, (1987) 15.
- 30 G. Weber, J. Runsink and J. Mattay, *J. Chem. Soc., Perkin Trans. I*, in the press.
- 31 J. Mattay, J. Runsink, R. Hertel, J. Kalbe and I. Schewe, *J. Photochem.*, in the press.
- 32 H. Beens and A. Weller, *Acta Phys. Pol.*, 34 (1968) 593.
- 33 D. Rehm and A. Weller, *Z. Phys. Chem., N.F.*, 69 (1970) 183.
- 34 M. Gordon and W. R. Ware (eds.), *The Exciplex*, Academic Press, New York, 1975: in particular see articles by T. Förster, A. Weller and N. Mataga.
- 35 D. Bryce-Smith, B. Foulger, J. Forrester, A. Gilbert, B. H. Orger and H. M. Tyrrell, *J. Chem. Soc., Perkin Trans. I*, (1980) 55.
- 36 A. Gilbert, G. N. Taylor, A. Collins, *J. Chem. Soc. Perkin Trans. I*, (1980) 1218.
- 37 P. de Vaal, G. Lodder and J. Cornelisse, *Tetrahedron Lett.*, 26 (1985) 4395.
- 38 A. Gilbert and P. Yianni, *Tetrahedron Lett.*, 23 (1982) 255.

- 39 A. Gilbert and P. Rodwell, *J. Chem. Soc., Chem. Commun.*, (1985) 1057.
- 40 N. J. Turro, J. McVey, V. Ramamurthy and P. Lechtken, *Angew. Chem.*, 91 (1979) 597; *Int. Ed. Engl.*, 18 (1979) 572.
- 41 D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 32 (1976) 1309; 33 (1977) 2459.
- 42 P. de Vaal, G. Lodder and J. Cornelisse, in S. M. B. Costa (ed.), *Proc. 11th IUPAC Symposium on Photochemistry, Lisbon, July 28 - August 1, 1986*, Centro De Quimica Estrutural, Instituto Superior Tecnico, Lisbon, 1986, pp. 312 - 313; *Tetrahedron Lett.*, 26 (1985) 4395.
- 43 N. C. Yang, R. L. Yates, J. Masnovi, D. M. Shold and W. Chiang, *Pure Appl. Chem.*, 51 (1979) 173.
- 44 N. C. Yang, J. Masnovi, W.-L. Chiang, T. Wang, H. Shou and D.-D. H. Yang, *Tetrahedron*, 37 (1981) 3285.
- 45 J. C. Berridge, A. Gilbert and G. N. Taylor, *J. Chem. Soc., Perkin Trans. I*, (1980) 2174.
- 46 T. S. Cantrell, *J. Org. Chem.*, 46 (1981) 2674.
- 47 J. C. Berridge, J. Forester, B. E. Foulger and A. Gilbert, *J. Chem. Soc., Perkin Trans. I*, (1980) 2425.
- 48 D. Bryce-Smith, W. M. Dadson and A. Gilbert, *J. Chem. Soc., Chem. Commun.*, (1980) 112.
- 49 H.-D. Scharf, H. Leismann, W. Erb, H. W. Gaidetzka and J. Aretz, *Pure Appl. Chem.*, 41 (1975) 581.
- 50 P. A. Wender and S. K. Singh, *Tetrahedron Lett.*, 26 (1985) 5987 and earlier reports.
- 51 J. Mani and R. Keese, *Tetrahedron*, 41 (1985) 5697 and earlier reports.
- 52 A. Gilbert and M. W. bin Samsudin, *J. Chem. Soc., Perkin Trans. I*, (1980) 1118.
- 53 A. Gilbert, G. N. Taylor and A. Collins, *J. Chem. Soc., Perkin Trans. I*, (1980) 1218.
- 54 H. C. Linstid, *Diss. Abstr. Int. B*, 39 (7) (1979) 3335.
- 55 E. M. Osselton, C. P. Eyken, A. W. H. Jans and J. Cornelisse, *Tetrahedron Lett.*, 26 (1985) 1577.
- 56 E. M. Osselton, E. L. M. Lempers and J. Cornelisse, *Rec. Trav. Chim. Pays-Bas*, 104 (1985) 124.
- 57 N. Al-Jalal, M. G. B. Drew and A. Gilbert, *J. Chem. Soc., Chem. Commun.*, (1985) 85.
- 58 E. M. Osselton, E. L. M. Lempers, C. P. Eyken and J. Cornelisse, *Rec. Trav. Chim. Pays-Bas*, 105 (1986) 171.
- 59 D. Bryce-Smith, W. M. Dadson, A. Gilbert, B. H. Orger and H. M. Tyrrell, *Tetrahedron Lett.*, 19 (1978) 1093.
- 60 A. Gilbert and P. Yianni, *Tetrahedron*, 37 (1981) 3275.
- 61 M. G. B. Drew, A. Gilbert and P. W. Rodwell, *Tetrahedron Lett.*, 26 (1985) 949.
- 62 M. G. B. Drew, A. Gilbert, P. Heath, A. J. Mitchell and P. W. Rodwell, *J. Chem. Soc., Chem. Commun.*, (1983) 750.
- 63 E. M. Osselton and J. Cornelisse, *Tetrahedron Lett.*, 26 (1985) 527.
- 64 D. Bryce-Smith, W. M. Dadson and A. Gilbert, *J. Chem. Soc., Chem. Commun.*, (1980) 112.
- 65 H. G. Viehe, R. Merenyi, L. Stella and Z. Janousek, *Angew. Chem.*, 91 (1979) 982; *Int. Ed. Engl.*, 18 (1979) 917 and references therein.
- 66 D. Bryce-Smith, *Chem. Commun.*, (1969) 806.
- 67 D. Bryce-Smith, *Pure Appl. Chem.*, 34 (1973) 193.
- 68 A. W. H. Jans, J. J. van Dijk-Knepper and J. Cornelisse, *Tetrahedron Lett.*, (1982) 1111.
- 69 J. Cornelisse, V. Y. Merritt and R. Srinivasan, *J. Am. Chem. Soc.*, 95 (1973) 6197.
- 70 A. W. H. Jans, B. van Arkel, J. J. Dijk-Knepper and J. Cornelisse, *Tetrahedron Lett.*, 23 (1982) 3827.
- 71 D. E. Reedich and R. S. Sheridan, *J. Am. Chem. Soc.*, 107 (1985) 3360.
- 72 T. S. Cantrell, *J. Org. Chem.*, 42 (1977) 4238.
- 73 N. Al-Jalal and A. Gilbert, *J. Chem. Research (S)*, (1983) 266.

- 74 D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, (1962) 2675.
75 A. Gilbert and P. Yianni, *Tetrahedron Lett.*, 23 (1982) 4611.
76 H. Leismann, J. Mattay, G. Schmitt and H.-D. Scharf, in E. Poquet *et al.* (eds.), *Proc. 9th IUPAC Symposium on Photochemistry, Pau, 1982*, Laboratoire de Chimie Structurale, Université de Pau et des Pays de l'Adour, Pau, 1982, pp. 206 - 207.
77 H. Leismann and G. Schmitt, in D. G. Whitten (ed.), *Proc. 10th IUPAC Symposium on Photochemistry, Interlaken, 1984*, Presses Polytechniques Romandes, Lausanne, 1984, pp. 435 - 436.
78 H.-G. Heine and W. Hartmann, *Angew. Chem.*, 87 (1975) 708; *Int. Ed. Engl.*, 14 (1975) 698.
79 A. Gilbert and P. Yianni, *Tetrahedron Lett.*, 23 (1982) 4611.
80 I. W. J. Still, T. S. Leong, *Tetrahedron Lett.*, 20 (1979) 1097.
81 A. Gilbert and G. N. Taylor, *J. Chem. Soc., Perkin Trans. I*, (1980) 1761.
82 J. Mani, J.-H. Cho, R. R. Astik, E. Stamm, P. Bigler, V. Meyer and R. Keese, *Helv. Chim. Acta*, 67 (1984) 1930.
83 G. C. R. Ellis-Davies, A. Gilbert, P. Heath, J. C. Lane, J. V. Warrington and D. L. Westover, *J. Chem. Soc., Perkin Trans. II*, (1984) 1833.
84 G. C. R. Ellis-Davies, A. Gilbert, J. V. Warrington and D. L. Westover, *J. Photochem.*, 27 (1984) 259.

Note added in proof

Some reports on meta photocycloadditions of arenes to olefins have been published recently since concluding this review:

- A. W. H. Jans, E. M. Osselton, C. P. Eyken, B. Griewel and J. Cornelisse, *J. Magn. Reson.*, 70 (1986) 169.
E. M. Osselton, E. S. Krijnen, E. L. M. Lempers and J. Cornelisse, *Recl. Trav. Chim. Pays-Bas*, 105 (1986) 375.
P. de Vaal, G. Lodder and J. Cornelisse, *Tetrahedron*, 42 (1986) 4585.
J. Cornelisse, A. Gilbert and P. W. Rodwell, *Tetrahedron Lett.*, 27 (1986) 5003.
P. A. Wender and K. Fisher, *Tetrahedron Lett.*, 27 (1986) 1857.