

THE INTER- AND INTRAMOLECULAR PHOTOCYCLOADDITION OF ETHYLENES
 TO AROMATIC COMPOUNDS

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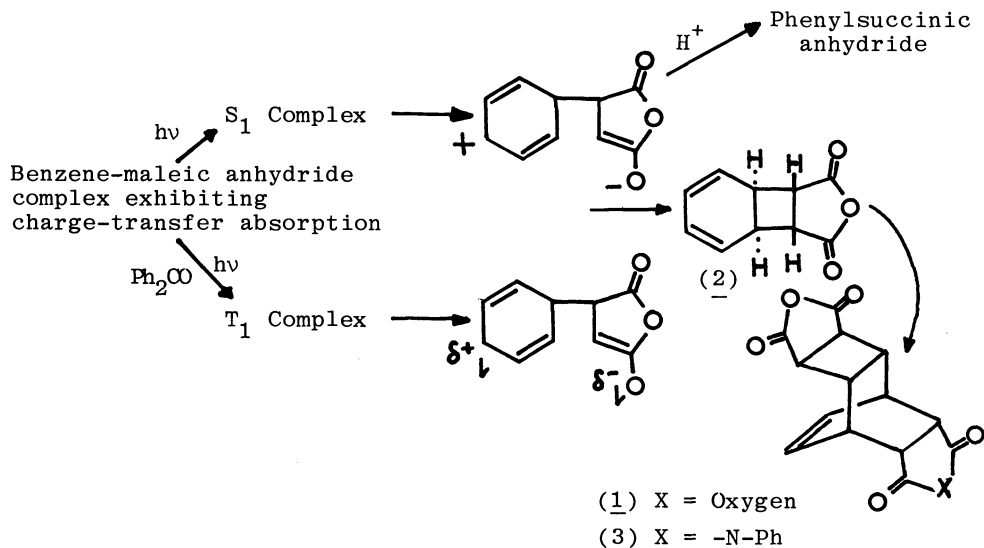
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Abstract - Dienophilic ethylenes yield solely *ortho* photocycloadducts with benzene whereas alkenes and enol ethers give products arising from both *ortho* and *meta* cycloaddition. The relative efficiencies of the two processes are largely predictable and this combined with reasonable chemical and quantum yields make these photoreactions realistic synthetic procedures towards bicyclo[4.2.0]octane and tricyclo[3.3.0.0^{2,8}]octane systems. The *ortho* cycloaddition involves a measure of charge-transfer to or from the ethylene at some stage in the reaction pathway, whereas two routes are considered to account for the orientational selectivity of the *meta* process involving ethylenes and substituted benzenes. Positions and modes of intramolecular reaction between the chromophores of non-conjugated phenyl vinyl bichromophoric systems are understandable in terms of their favoured molecular conformations leading to preferred orientations of the addends.

INTRODUCTION

The current wide-spread interest in the photocycloaddition reactions of aromatic systems with ethylenes, dienes and acetylenes (Ref. 1 & 2) has its origin in the observation, reported twenty years ago, that ultraviolet irradiation of benzene solutions of maleic anhydride yielded the 1:2 adduct (1) (Ref.3). Several groups of workers have since described a variety of aspects of this reaction and formation of (1) has been demonstrated to arise from irradiation within the charge-transfer absorption band of the addend complex (Ref.4), to be sensitised by compounds with a triplet energy greater than 66 kcal/mole (Ref.3c,4, & 5), to proceed via the non-isolated 1:1 *ortho* cycloadduct (2) (Ref.6), and to be diverted by a proton source (Ref.7) or N-phenylmaleimide (Ref.8) to yield phenylsuccinic anhydride or the 1:1:1 adduct (3) respectively. Scheme 1 below summarises the results of the mechanistic studies into this system.

Scheme 1

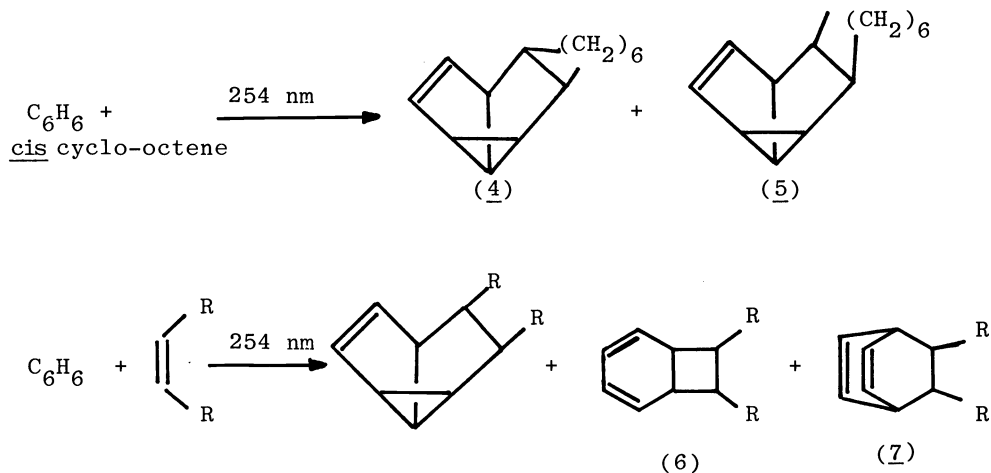


Certain maleimides (Ref.4,9 & 10) and dienophilic acetylenes (Ref.11) also yield ortho cycloadducts with benzene but in these cases the reaction proceeds by attack of the photoexcited addend onto the arene.

This paper will be concerned with inter- and intramolecular benzene-ethylene photoaddition reactions which result from 254 nm radiation and which involve exclusively the initial excitation of the arene.

INTERMOLECULAR BENZENE-ETHYLENE SYSTEMS

Early investigations of the photoreactions of benzene with acyclic and cyclic alkenes which could not be electronically excited under the experimental conditions and which did not form complexes with the arene having charge-transfer absorption, revealed a novel and intriguing process which with, for example, benzene and cis cyclo-octene led to the formation of the exo and endo meta cycloadducts (4) and (5) respectively (Ref.12 & 13). Consistent with these observations, it was deduced from an orbital symmetry analysis of cycloadditions of ethylenes to the benzene ring (Ref.14), that the meta cycloaddition was the only "allowed" concerted process from the S_1 state ($^1B_{2u}$) of the arene, and indeed this state was subsequently shown by Cvetanovic and co-workers (Ref.15) to be that involved in the addition process. More detailed studies of such systems have shown that, dependent upon the particular alkene, meta cycloaddition is the exclusive route or may be competitive with the other two possible cycloaddition pathways which lead to the ortho (6) and para (7) cycloadducts (Ref.16,17 & 18): in many systems para cycloaddition is not observed and for all additions but that of 1,2-dienes (Ref.19) is the least efficient of the three reactions. The lack of detection of products of types (6) and (7) in previous studies is probably simply a reflection of their greater photolabilities than the meta cycloadducts (Ref.16 & 17). It is important to note here that in all three modes of cycloaddition the stereochemistry of the alkene is preserved in the product (Ref.16) thereby implying a concerted process: the S_1 state of benzene is again considered to be that involved in the ortho and para cycloaddition reactions. In order to circumvent the dictate from orbital

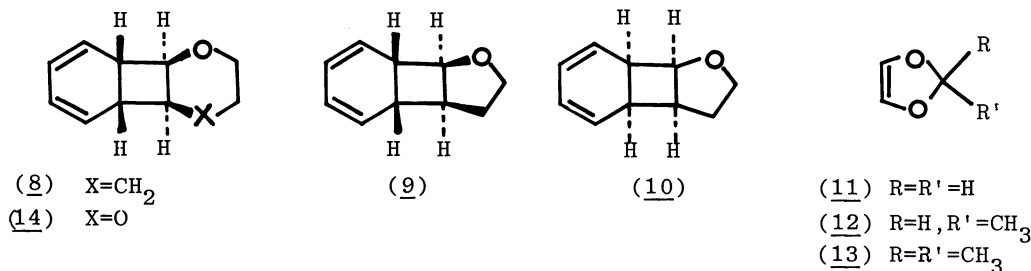


symmetry analysis that formation of the adducts (6) and (7) is formally forbidden as a concerted process from S_1 benzene and S_0 alkene (Ref.14 & 20), an excited state complex between these species was proposed as the reaction intermediate which led to the observed products (Ref.16). The involvement of an exciplex both as a precursor of the ortho and para products and of the meta cycloadduct found support from theoretical considerations (Ref.21) and experimental evidence was provided by the study of the intramolecular photoreactions of cis and trans 6-phenylhex-2-enes (see later) for this proposal in the case of the last named mode of reaction (Ref.22).

A systematic survey of the photoreactions of a wide variety of ethylenes with benzene and its simple derivatives has revealed, for these reactions, a number of important features which are of predictive value concerning selectivities of the modes of cycloaddition and stereo- and regio-chemistries (Ref.18 & 23). Studies with the C_5 - C_9 cyclic alkenes (see Table 1) show that

the major reaction appeared quite definite (Ref.23). The exceptions to this original proposal are few but significant (Ref.28) and we now note that these values are too restrictive. Nonetheless from our studies and those of others (Ref.24 & 29) it can be deduced firstly, that ethylenes with ionisation potentials closely similar to that of benzene will preferentially or exclusively undergo meta cycloaddition to the arene, and secondly that in all cases in which ortho cycloaddition is the favoured or sole reaction mode, the ethylene is a relatively powerful electron donor or acceptor as judged by ionisation potentials or electron affinities: the photoaddition of vinylene carbonate to benzene provides the exception to the converse of both of these statements (Ref.28).

As noted above by the data in Table 2, there appears to be a well-defined trend between ionisation potential differences of the addends and preferred modes of cycloaddition within a series of ethylenes, but our studies of systems involving enol ethers demonstrate that structural features of the ethylene may play a vital role in determining the overall selectivity of the reaction (Ref.25). For example irradiation of benzene solutions of 2,3-dihydropyran gives a product mixture of which the exo ortho cycloadduct (8) comprises 95% whereas, in contrast, from the reaction involving 2,3-dihydrofuran, a mixture of 1:1 adducts results, the major isomers of which are the exo and endo ortho cycloadducts (9) and (10) respectively. The exo product (9) is relatively photolabile compared to the endo stereomer (10) and their photostationary ratio is ca. 1:12 respectively. The ratio of the efficiency of ortho to meta cycloadduct formation from the 1,3-dioxoles (11), (12), and (13) with benzene varies with ionisation potential but in a manner similar to that described above for methylethylenes. Thus the respective ratios of ortho to meta cycloaddition for (11), (12), and (13) which have ionisation potentials of 8.56, 8.36, and 7.92 eV respectively are 21:38, 1:1, and 2:1 (Ref.29). On the other hand, the reaction of benzene with 1,4-dioxen (ionisation potential 8.54) is again highly selective giving greater than 98% of the exo ortho cycloadduct (14) (Ref. 25). Thus for the pairs 1,3-dioxoles and 1,4-dioxen, and 2,3-dihydrofuran and 2,3-dihydropyran, there is apparently no correlation between ionisation potential and selectivity of reaction: the overall quantum yields for both systems are of the same order. The only obvious feature in these systems is that the 5-membered rings yield both ortho and meta cycloadducts whereas the



former type of product is formed almost exclusively from the 6-membered ring ethenyl ethers. In contrast, although cyclopentene undergoes meta cycloaddition to benzene with a reasonable efficiency ($\phi = 0.2$) (Ref.18 & 30), the reaction with cyclohexene is very inefficient and cyclobutane dimers of the ethylene formed from T₁ benzene sensitisation are significant components of the reaction mixture (Ref. 18). Thus the ethylene features which control reaction efficiencies and selectivities are clearly very subtle and may involve minor steric interactions of the addends.

The stereochemistry of the ortho and meta photocycloadditions of ethylenes to benzene requires comment. It has been shown that the ortho cycloadditions of cis cyclo-octene (Ref.31), cis but-2-ene (Ref.16), maleic anhydride (Ref.32), and maleimides (Ref.9) to benzene are stereospecific, the former two have endo stereochemistry whereas only the exo isomers are formed from the latter two ethylenes. A search for ground state complexes in these and other ethylene-benzene systems by ¹H n.m.r. spectroscopy revealed apparent preferred orientations of association of the addends (Ref. 4 & 33): ethylenes which could be considered as having electron donor properties relative to benzene were deduced to be oriented in an endo relationship whereas the dienophilic ethylenes appeared to prefer an exo orientation. The stereochemistry (where known) of the ortho adducts thus seemed to be a remarkable reflection of preferred orientations of the addends in the

the overall efficiency of the addition process and the relative efficiency of the formation of the ortho and meta 1:1 cycloadducts are very dependent upon the particular system (Ref.18).

TABLE 1. Photocycloaddition of cyclic alkenes to benzene

Alkene	Type of adduct with benzene (ϕ)	Alkene ionisation potential eV
<u>trans</u> Cyclo-octene	<u>ortho</u> (0.37), <u>meta</u> (0.14,0.14)	8.51
<u>cis</u> Cyclo-octene	<u>ortho</u> (0.09), <u>endo meta</u> (0.31) <u>exo meta</u> (0.07)	8.75
<u>cis</u> Cyclononene	<u>endo meta</u> (0.13), <u>exo meta</u> (0.02) two further 1:1 adducts of unknown structure (0.02 combined)	8.78
Cycloheptene	<u>endo meta</u> (0.16), <u>exo meta</u> (0.11) (+ minor amounts of alkene dimer)	8.86
Cyclohexene	Very low yields (< 0.001) of 1:1 adduct and alkene cyclobutane dimers	9.12
Cyclopentene	<u>endo meta</u> (0.17), <u>exo meta</u> (0.02) (+ minor amounts of alkene dimers)	9.18

There is, however, the trend that the ratio of efficiency of the ortho to meta cycloaddition increases with increase in electron donor property, as measured by ionisation potential, of the alkene. The same trend is also observed with methylethylenes (Table 2) and enol ethers generally undergo ortho more efficiently than meta cycloaddition to benzene (Ref.25).

TABLE 2. Photocycloaddition of ethylene and methylethylenes to benzene

Alkene	$\text{CH}_2=\text{CH}_2$ (Ref.24)	$\text{CH}_2=\text{CHMe}$ (Ref.24)	$\text{CH}_2=\text{CMe}_2$	<u>cis</u> $\text{MeCH}=\text{CHMe}$ (Ref.16)	$\text{MeCH}=\text{CMe}_2$	$\text{Me}_2\text{C}=\text{CMe}_2$
<u>ortho:meta</u> cycloaddition ratio	1:1	<u>meta</u> only	<u>meta</u> only	1:7	1:4	8:1
Alkene ionisation potential eV	10.5	9.73	9.24	9.13	8.67	8.3

Further, dienophilic ethylenes (electron acceptors) such as acrylonitrile, methyl acrylate, or methyl vinyl ketone which do not exhibit charge-transfer complex absorption with benzene, yield exclusively ortho cycloadducts (Ref.26). These data and the fact that the efficiency of the ortho process is generally increased in polar solvents (Ref.23) whereas that of the meta cycloaddition is essentially unaffected by change of this parameter (Ref.23 & 27) lead us to propose that, in agreement with the orbital symmetry analysis, the former reaction has an element of charge-transfer to or from the ethylene at some stage during the reaction pathway whereas the meta cycloaddition is essentially homopolar. From none of the foregoing systems has fluorescence emission been observed which may be attributable to that from an excited complex of the addends.

At one time it did appear that the value of the ethylene ionisation potential may be used to indicate the preferred mode of cycloaddition to benzene and the "cut off" values of >9.6 and <8.65 eV at which the ortho process became

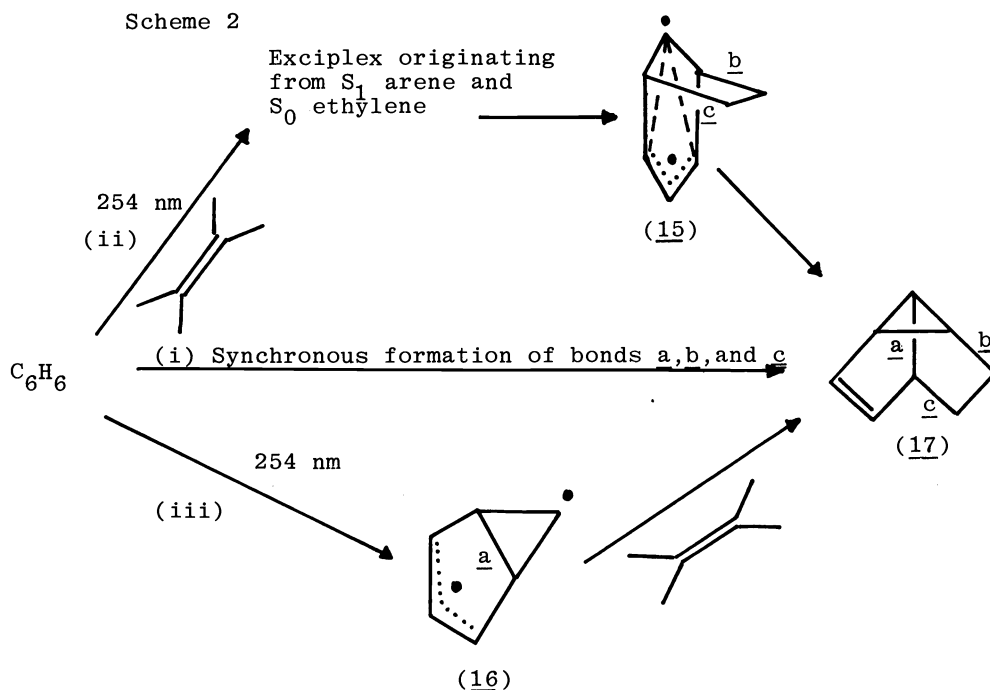
ground state. We have examined the predictive value of this concept by the determination of the stereochemistry of a number of ortho cycloadducts of benzene with ethylenes of varying electron donor-acceptor properties: the results are summarised in Table 3 from which it will be seen that with

TABLE 3. Stereochemistry of ortho photocycloaddition of ethylenes to benzene

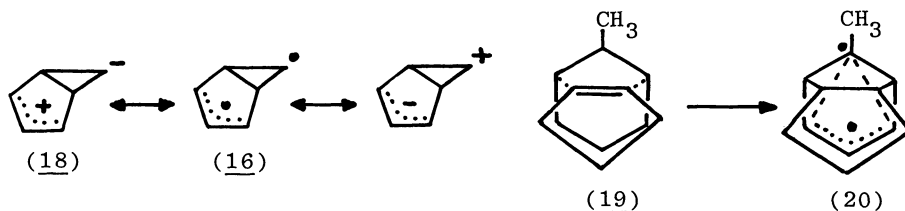
Ethylene	Stereochemistry
Maleic anhydride	<u>exo</u>
Maleimide(s)	<u>exo</u>
Acrylonitrile	<u>exo</u>
Methacrylonitrile	<u>exo:endo</u> (CN) 6:5
Methyl acrylate	<u>exo:endo</u> 2:1
Methyl methacrylate	<u>exo:endo</u> (CO ₂ Me) 2:1
Methyl vinyl ketone	<u>exo:endo</u> 1:1
<u>cis</u> Cyclo-octene (Ref.31)*	<u>endo</u>
Vinyl acetate*	<u>endo</u>
But-2-ene (Ref.16)*	<u>endo</u>
Ethyl vinyl ether	<u>exo</u>
2,3-Dihydrofuran	<u>exo:endo</u> 3:5
2,3-Dihydropyran	<u>exo</u>
1,3-Dioxole (Ref.29)*	<u>exo</u>
1,4-Dioxene	<u>exo</u>

* meta Cycloaddition major reaction pathway

the exception of the systems involving cis-cyclo-octene, but-2-ene, and vinyl acetate, exo stereomers are formed in all cases and there are examples both of electron donor and acceptor ethylenes in which the ortho cycloaddition process lacks selectivity yielding both exo and endo isomers. Thus preferred ground state orientations of the addends, as deduced from ¹H n.m.r. spectroscopy has little or no influence on the stereochemistry of the ortho cycloaddition process. The involvement of exciplexes in ortho cycloadditions of ethylenes to benzene is still largely a matter of speculation but all that is known of the process is not inconsistent with such a proposal.

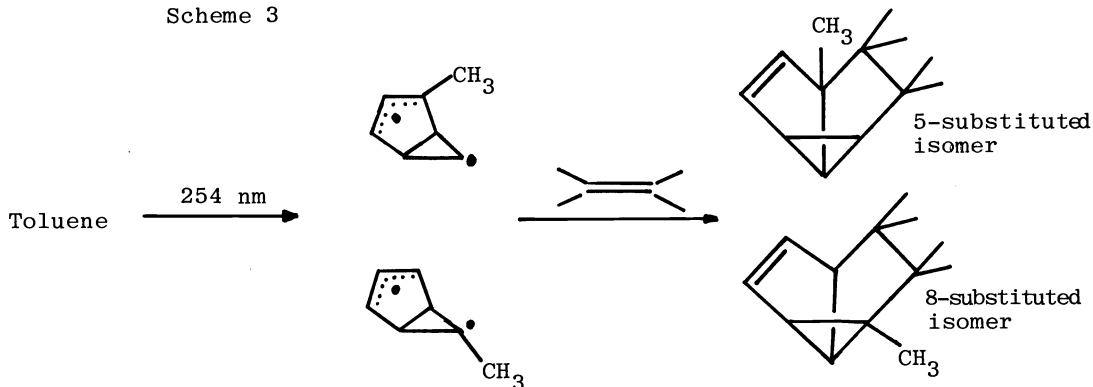


The meta cycloaddition favours the formation of endo stereomers and in some systems these are the sole products: this aspect of the reaction is relevant to mechanistic considerations for the reaction. In principle there are three plausible pathways for the process: these are (i) synchronous formation of all three new bonds a, b, and c, (ii) meta addition of the ethylene to the arene to yield (15), possibly resulting from collapse of an excited state complex, followed by formation of the ethenyl cyclopropane system, and (iii) prior meta bonding within the benzene ring to give the species (16) which undergoes addition to the ethylene to give (17) (see Scheme 2) and which could also be envisaged as the precursor of fulvene and benzvalene. It has been noted that S_1 benzene is potentially meta bonding and may form (16) adiabatically (Ref.34): the species (16) may be better represented as a hybrid between dipolar canonical forms with (18) being likely to contribute most to the hybrid. The "allowedness" of the addition process from orbital symmetry considerations is seemingly insensitive to such mechanistic details as which of the routes outlined in Scheme 2 is preferred (Ref.1 & 20). At one time, we favoured route (iii) for the formation of (17) for essentially two reasons. Firstly, it is known that the quenching of the arene fluorescence by alkenes is weak and little more than that of alkanes (Ref.35), and consistent with this, in pathway (iii) there is no formal interaction between S_1 benzene and the ethylene. It is, however, worth noting here that the quenching of benzene fluorescence by ethylenes increases with the latter's increase in electron donor characteristics and in such systems, as described above, the ortho cycloaddition efficiency increases relative to that of the meta process: this is consistent with the proposal that the former reaction arises via interaction of the ethylene with the S_1 arene. Secondly, the formation of fulvene from irradiated benzene is quenched by the presence of an alkene and one interpretation of these facts together is that the isomerisation and meta adduct formation share a common intermediate. However, arene fluorescence quenching in phenyl vinyl bichromophoric systems is very efficient and from a study of cis and trans 6-phenylhex-2-enes, Morrison and co-workers deduced that the intramolecular meta photocycloaddition arose via an exciplex route (i.e. pathway (ii)) and suggested that their results could be extended to the intermolecular process (Ref.22). Experimental support for the latter proposal has been provided from studies of the orientational and stereochemical selectivities of the meta cycloaddition of a variety of 1,2-disubstituted acyclic and cyclic alkenes to methyl and methoxy benzenes (Ref.36). Thus the observed locospecific endo 2,6-addition was rationalised by the involvement of an endo sandwich exciplex, for example (19)

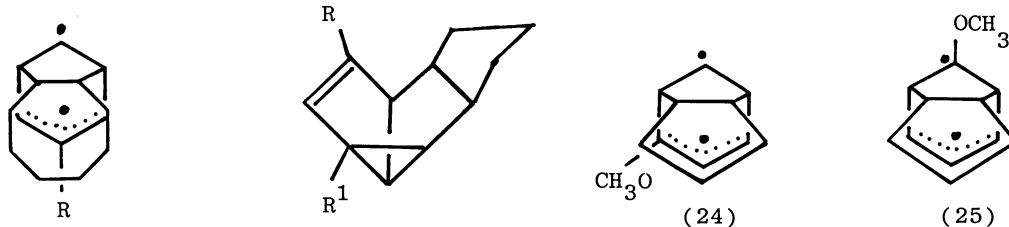


between toluene and cyclopentene, and the addition intermediate (20): it was considered that the "last bond to close is the cyclopropane which seems to form in either way". If substituent stabilisation of radical/charge centres in these reactions is important, then the pathway involving prior meta bonding in the arene to form (16), would yield the 8- and 5-substituted isomers from toluene as shown in Scheme 3. Steric factors of the arene substituent cannot be ignored and in the attack of an ethylene onto the precursor of the 5-isomer, such aspects may predominate and result in the formation of the 3-substituted isomer of (17). Little selectivity in the formation of substituted meta adduct isomers from benzene derivatives may be expected in a process involving synchronous formation of bonds a, b, and c. Our investigations also demonstrate the selectivity of the meta cycloaddition but show that there is not a unique pathway to the products: the positional isomer(s) obtained from the reaction depend upon the particular arene and ethylene and for some systems this reflects the involvement of species (16) and route (iii) (Ref.37). Thus for example the irradiation of toluene and cis cyclo-octene yields the isomer of (17) with the methyl group in the 5-position and the 8-methoxy compound is formed from anisole and cis cyclo-octene: both results suggest that route (iii) is the exclusive pathway to the meta adduct in these examples. Further, although the

Scheme 3



1-substituted isomers are obtained from *cis* cyclo-octene and *isopropyl*benzene and *t*-butylbenzene, the 3-isomer constitutes 30 and 60% respectively of the adduct mixtures. An intermediate of type (15) can account for the 1-isomers but it is considered that the formation of the 3-substituted compounds from this formal 3,5-addition is rationalised better on steric grounds and substituent stabilisation of radical centres, by the involvement of a species of type (16) than by (21). The steric influence on the *meta* cycloaddition is further demonstrated by the respective 5:1 ratio of the formal 3,5-attack product to that resulting from 2,6-attack in the *cis* cyclo-octene-*p*-methylcumene system. Re-examination of selected systems described in Ref.36 has confirmed the comparability of experimental conditions and methods of product detection and isolation used in the two studies. The only small discrepancy we have observed is in the anisole-cyclopentene system: this yields as well as the previously described 1-substituted isomer of (17), two further *meta* cycloadducts which combined constitute 8% of the reaction mixture and to which the structures (22) and (23) are assigned. Formation of these two isomers may be rationalised by the intermediate (24) which would be expected to be far less favoured on steric grounds than the proposed precursor (25).

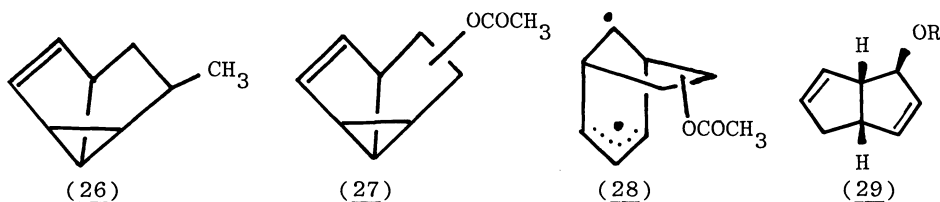


(21) R = *isopropyl*
or *t*-butyl

(22) R=OMe, R¹=H
(23) R=H, R¹=OMe

Our results along with those described in Ref.36 show that there is not a unique mechanism for the *meta* cycloaddition process but the results may be reasonably interpreted by the involvement of the species (15) and/or (16) which imply pathways of initial *meta* addition probably resulting from an exciplex, and prior *meta* bonding in the arene respectively. The results of the studies do, however, pose the important question "In systems which undergo addition by the exciplex route, is a greater degree of arene fluorescence quenching by the ethylene observed than in those which are deduced to proceed via initial *meta* bonding in the benzene derivative?" As yet this question remains unresolved as the results at present lack the essential consistency for a definite answer and despite many studies by ourselves and almost certainly others, the only benzene-ethylene systems from which exciplex emission has been observed involve 1,2-dialkoxyethylenes at high addend concentrations in acetonitrile solution (Ref.38): in the case of 2,2-dimethyl-1,3-dioxole, the quenching of this emission by triethylamine has been reflected by a similar reduction in *meta* cycloadduct formation (Ref.29).

There is another aspect of the *meta* photocycloaddition which is relevant to the foregoing mechanistic considerations. The reaction with benzene has been largely studied with 1,2-disubstituted alkenes which cannot reflect any regioselectivity of the process. Some selectivity may be expected in the addition of a vinyl compound if species (18) is involved to any extent in the reaction pathway to (17). On the other hand, if (15) is the intermediate, then it is not considered that the vinyl substituent would exert a significant directing influence on the final bond closure and little or no regioselectivity would be observed. Similarly for route (i) in Scheme 2 a random distribution of regioisomers may be expected. Propene has been reported to yield only the 7-methyl isomer (26) with benzene (Ref.24) whereas from isobutylene the 6,6- and 7,7-dimethyl isomers are formed in approximately equal amounts (Ref. 18). A further aspect of the reaction influenced our choice of system to study the regioselectivity feature. The *meta* cycloaddition of ethylenes to benzene and its simple derivatives is an excellent one step route to the dihydrosemibullvalene skeleton and has been used as a step towards the stereospecific synthesis of perhydroazulenes (Ref.39). Chemical and quantum yields of the addition are good for many systems and the extent of side reactions such as the *ortho* reaction is to some extent predictable. Nonetheless the opportunity to exploit the *meta* cycloadduct formation in synthesis is restricted since only hydrocarbon ethylenes and vinyl ethers appear to react in this mode. We have made a study of the benzene-vinyl acetate system in order to assess the involvement of the polar intermediate (18) in the process and in an attempt to functionalise the dihydrosemibullvalene system (Ref.40). Irradiation of mixtures of the addends gave the *meta* and *ortho* cycloadducts in a 7:1 ratio consistent with that predicted from the ethylene ionisation potential concept proposed earlier (Ref.23). The *ortho* product was isolated as its N-phenylmaleimide Diels-Alder adduct and was shown to have specifically *endo* stereochemistry. The 7-*endo*, 7-*exo*, 6-*endo*, and 6-*exo* acetoxy isomers of the *meta* cycloadduct (27) were deduced to be formed in the approximate respective ratios of 20:1:6:6. The polarised intermediate (18) would be expected to yield the 7-substituted isomers selectively and hence assuming that the alternative intermediate (28) yields equal amounts of the 6- and 7-acetoxy derivatives of (27), then it would appear that approximately 25% of the reaction may proceed by a pathway which involves the former species but it is not obvious why equal amounts of the two 6-acetoxy stereoisomers are produced whereas formation of the 7-*endo* isomer is greatly favoured in comparison to the 7-*exo* adduct. Elimination of acetic acid from the acetates (27) under electron impact is a facile process but the *meta* cycloadducts are essentially photostable. Attempts to dehydrate the derived alcohols to semibullvalene have proved inefficient or unsuccessful but interestingly treatment of alcoholic solutions of (27) with trace amounts of acids efficiently yields



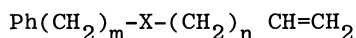
2-alkoxybicyclo[3.3.0]octa-3,7-dienes (29) which are known to be formed from similar treatment of this C_8H_8 isomer (Ref.41).

NON-CONJUGATED PHENYL-VINYL BICHROMOPHORIC SYSTEMS

As noted above, the first experimental evidence for the intermediacy of excited state complexes in *meta* cycloaddition was provided from a study of the intramolecular photocyclisation of the 6-phenylhex-2-enes (Ref.22). In view of the importance of this result, the considerable activity in the area of intermolecular arene-ethylene photoreactions (Ref.1&2), and the wide general interest in intramolecular interactions and reactions of non-conjugated bichromophoric molecules (Ref.42), it is surprising that this

study and a description of the photoprocess with the thermal adduct of 1,4-naphthoquinone and cyclopentadiene (Ref.43) were the only two published accounts which reported examples of the intramolecular cycloaddition at the commencement of our work in this area. We extended our studies of the intermolecular systems described above into those of the corresponding intramolecular compounds in order to obtain further information concerning the significant features of benzene-ethylene photoreactions in particular and the factors which may influence the photo-lability or stability of non-conjugated bichromophoric compounds in general. Thus it was of interest to ascertain if relative electron donor-acceptor properties of the chromophores would be a significant factor in determining the mode of intramolecular cyclisation and how the mode of reaction and positions of ethylene attack onto the phenyl group would be affected by the number and type of intervening units between the chromophores and the preferred conformations of the molecule.

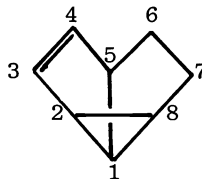
In order to achieve our objectives we have made a study of the photochemistry of non-conjugated phenyl vinyl bichromophoric systems of type (30) but only in one case was the number of units between the chromophores greater than four (Ref.44). Vinyl compounds were chosen for study as, although in general they undergo photoadditions to benzene less readily than 1,2-disubstituted ethylenes, such systems avoid problems arising from photosensitised cis-trans isomerisation and possible differing photoreactivities of the geometrical isomers. In view of this and since interaction between the chromophores of non-conjugated bichromophoric systems is maximised when the number of intervening units is three (Ref.45), the hydrocarbon "standard" with which the other systems were compared was 5-phenylpent-1-ene. As will be seen, meta cycloaddition is a significant or major mode of reaction for most of the systems which were found to be photoreactive. Numbering of such products is that given in (31) and it should be noted that the unit originally joining the chromophores must now reside between the 6- or 7-positions and the 1-,2-,3-,4-,5-, or 8-positions. There are several ways in



where 'm' and/or 'n' = 0,1, or 2

X = $-\text{CH}_2-$, oxygen, N-CH_3 , $-\text{O-CO-}$, $-\text{CO-O-}$

(30)

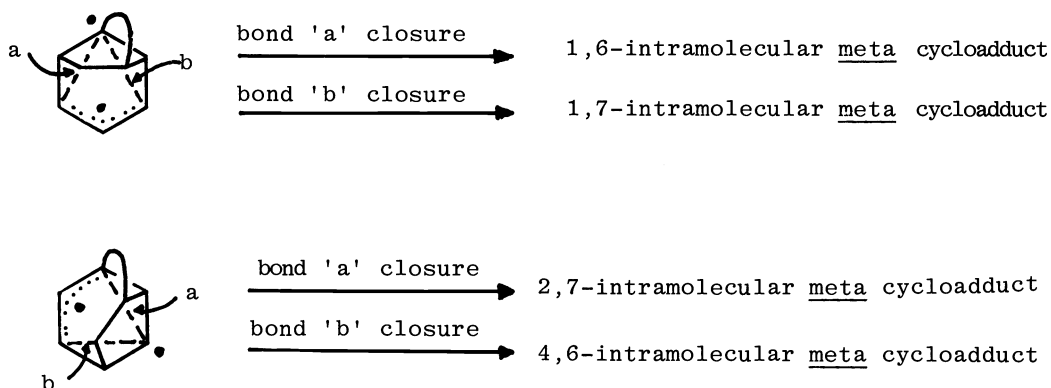


(31)

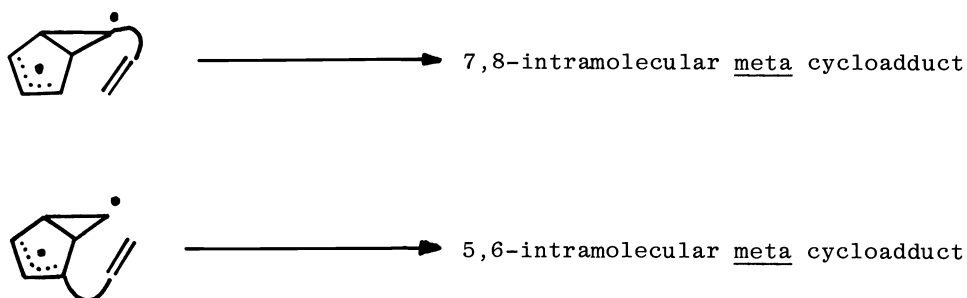
principle in which the meta cycloaddition may occur but molecular models show that because of steric and strain constraints in the product imposed by the intervening chain originally between the chromophores, some isomers simply cannot be formed unless the chain has greater than five units. For three units between the chromophores, only the intramolecular meta adducts involving the 1,6-, 1,7-, 4,6-, 5,6-, and 7,8-positions in (31) are considered to be feasible: these isomers reflect attack of the ethylene onto the phenyl group at the 2,6-positions for the first two, the 1,3-positions for the latter two, and the 2,4-positions for the 4,6-isomer. As shown in Schemes 4 and 5 from an analysis of these likely isomers in terms of the mechanistic arguments based on substituent stabilisation of radical/charge centres for meta cycloaddition, the first three isomers may be rationalised by an initial meta cycloaddition whereas prior arene rearrangement would appear to account for the latter two isomers.

Morrison and co-workers had shown that cis 6-phenylhex-2-ene underwent 1,3-addition to yield the 5,6- and 7,8- exo isomers of (31) whereas only 2,6-addition occurred in the trans isomer to give the 1,6- exo product: molecular models indicate that in this and the other systems (30), this isomer would be formed in preference to the 1,7- exo isomer produced by the alternative mode of cyclopropane ring closure. In view of the reasonings behind Schemes 4 and 5, it is a matter of concern that from photophysical studies of cis 6-phenylhex-2-ene, excited state complexes were judged to be precursors of the addition and yet the products of the reaction are not those expected by this route. It may well be that in intramolecular systems the approach argued from intermolecular cases is too simplistic and the importance of substituent stabilisation of intermediates is eclipsed by, for example, conformational features of the molecule. Our studies with 5-phenylpent-1-ene and the ethers (30) are summarised in Table 4 and inspection of these data

Scheme 4



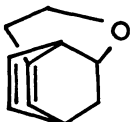
Scheme 5

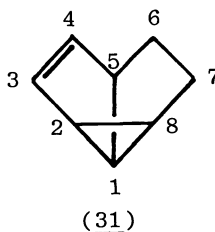


reveals several interesting features of these reactions. Thus although a decrease in reaction efficiency in going from three to four intervening units as in 5-phenylpent-1-ene and 6-phenylhex-1-ene and as in phenethyl vinyl ether and 3-phenylpropyl vinyl ether may have been expected, the change in reaction mode in the latter examples is most noteworthy. 5-Phenylpent-1-ene and the ethers phenethyl vinyl ether, benzyl allyl ether, and 4-phenoxybut-1-ene display significantly different photochemistries and illustrate that the number of intervening units between the chromophores, although important, is not the sole feature of bichromophoric systems which can markedly influence the efficiency and mode of reaction. In phenyl-vinyl non-conjugated systems at least, relative electron donor-acceptor properties of the chromophores appear also to be one significant feature which may determine the efficiency of product formation, the extent of side reactions (principally polymerisation), the mode of reaction, and the preferred orientation of attack. Nonetheless other factors may be operating as from knowledge of analogous intermolecular systems, ortho cycloadditions were to be expected for the vinyl ethers and it is necessary to account for the relatively efficient formation of the normally disfavoured para cycloaddition mode of reaction observed for phenethyl vinyl ether.

Space-filling molecular models of the non-conjugated phenyl vinyl bichromophoric ethers and hydrocarbons reveal that some conformations of the molecules are more favoured than others which leads to preferred orientations of the two chromophores. In no case under study, however, is an ortho (1,2- or 2,3-) approach of the vinyl group onto the phenyl moiety the favoured orientation. With phenethyl vinyl ether, the conformation in which interaction between the two chromophores appears maximised and the ethane hydrogens are non-eclipsed is that shown in (32) in which the vinyl group has an orientation between the 1, 3- and 2,5-phenyl positions with a bias towards the latter configuration: this orientation of interaction deduced from models is a reflection of the positions of photocycloaddition. Similarly for benzyl allyl ether the preferred orientation is seemingly that

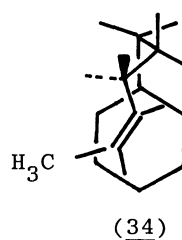
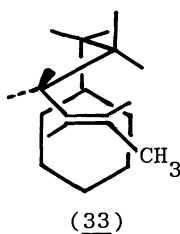
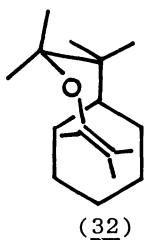
TABLE 4. Intramolecular photocyclisation of phenyl-vinyl bichromophoric systems

Compound	Position of attack	Substituted positions in meta cycloadduct (31)	Quantum yield
$\text{Ph}(\text{CH}_2)_3\text{CH}=\text{CH}_2$	2,6-	1,6-	0.11
	1,3-	5,6-	0.023
		8,7-	0.02
$\text{Ph}(\text{CH}_2)_4\text{CH}=\text{CH}_2$	1,3-	5,6-:8,7- 1:1	<0.005 total
$\text{PhCH}_2\text{-O-CH}_2\text{CH}=\text{CH}_2$	2,6-	1,6-	0.017
	1,3-	5,6-	0.02
		8,7-	0.03
$\text{Ph}(\text{CH}_2)_2\text{-O-CH}=\text{CH}_2$	2,5-		0.23
	1,3-	5,6-	0.006
$\text{Ph-O-(CH}_2)_2\text{-CH}=\text{CH}_2$	2,4-	4,6-	<u>a</u>
$\text{Ph-(CH}_2)_3\text{-O-CH}=\text{CH}_2$	1,3-	5,6	0.005
		8,7-	0.007
	2,4-	4,6-	0.05



a Excessive polymer deposits and very inefficient intramolecular cycloaddition prevented meaningful ϕ measurements.

in which the vinyl group resides in approximately 1,3- and 2,6- locations and in 3-phenylpropyl vinyl ether the 2,4-positions appear to be those most accessible to the vinyl group for the conformation in which the hydrogens in the propane chain are staggered. It must be admitted, however, that not in all cases examined is there a "match" between preferred orientation of the chromophores and observed photochemical addition of the vinyl onto the phenyl group. Nonetheless such a simple analysis by molecular models does predict the 2,6-intramolecular cycloaddition (33) for *trans* 6-phenylhex-2-ene and a corresponding 1,3-reaction (34) for the *cis* isomer. Thus conformational aspects of non conjugated phenyl vinyl bichromophoric molecules appear to be a dominant directing feature in their intramolecular cycloadditions.



The absorption spectra of the compounds in the present study are unexceptional and in no case is fluorescence emission attributable to an exciplex observed. The arene fluorescence is, however, quenched with varying degrees of efficiency by the vinyl group and these results are summarised in Table 5. Increase in the quenching of the arene fluorescence by the vinyl

TABLE 5. Fluorescence emission of phenyl-vinyl bichromophoric systems relative to npentylbenzene *

$\text{Ph}(\text{CH}_2)_3\text{CH}=\text{CH}_2$	0.08
$\text{Ph}-\text{CH}_2-\text{O}-\text{CH}=\text{CH}_2$	0.02
$\text{Ph}-\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$	0.50
$\text{PhCH}_2\text{OCH}_2\text{CH}=\text{CH}_2$	0.15
$\text{PhCH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$	0.50
$\text{Ph}(\text{CH}_2)_2\text{OCH}=\text{CH}_2$	0.05
$\text{Ph}(\text{CH}_2)_2\text{OCH}_2\text{CH}_3$	0.85
$\text{Ph}(\text{CH}_2)_3\text{OCH}=\text{CH}_2$	0.40
$\text{Ph}(\text{CH}_2)_3\text{OCH}_2\text{CH}_3$	0.85
$\text{Ph}-\text{O}-(\text{CH}_2)_2-\text{CH}=\text{CH}_2$	0.3 †

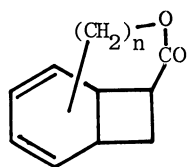
* Determined using comparative peak heights at 284 nm for 0.0004M solutions in iso-octane.

† Relative to anisole using comparative peak heights at 290 nm.

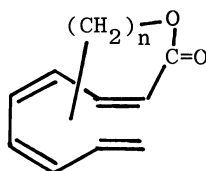
group is generally reflected in an increase in the efficiency of the intramolecular cycloadduct formation which is consistent with a route involving interaction of the chromophores in the excited state and not with one of prior arene rearrangement followed by ethylene addition. There is, however, an interesting detail from the fluorescence and quantum yield data of benzyl allyl ether and 5-phenylpent-1-ene which requires comment. In both systems the quantum yield of 1,3-cycloaddition is approximately the same although that of the 2,6-reaction is some six-fold lower for the ether than the hydrocarbon. Both systems show quenching of the arene fluorescence by the vinyl group but this is more pronounced for 5-phenylpent-1-ene than benzyl allyl ether and in this latter case it may well be that a contributing factor to the observed quenching, as evidenced by the result with benzyl ethyl and benzyl propyl ethers, is through bond interaction between the phenyl and ethereal oxygen, a feature which has received comment in other systems (Ref.46). Thus in benzyl allyl ether in which the excited state interaction is the weaker as judged by fluorescence quenching, only the 2,6-mode of reaction is significantly reduced whereas the efficiency of the 1,3-process is essentially the same as that of 5-phenylpent-1-ene. It is tempting to suggest that in some systems the low efficiency 1,3-intramolecular cycloaddition may result from prior arene rearrangement as shown in Scheme 5 and that not all adducts result from interaction between the S_1 benzene and S_0 ethylene.

The non-conjugated phenyl vinyl bichromophoric systems with ester and amine moieties in the intervening units are remarkably photostable and in most cases only undergo low efficiency cleavage reactions. Based on the ortho photoaddition of methyl acrylate to benzene (Ref.26), it may have been expected that compounds $\text{Ph}(\text{CH}_2)_n\text{OCOCH}=\text{CH}_2$ would yield intramolecular ortho cycloadducts (35) but the only evidence for such a mode of reaction was the appearance of absorptions in the 310-370 nm region of the spectrum which may be attributed to the ring-opened products (36). From known extinction coefficients of such tetraene systems, it is assessed that <0.001% of the starting bichromophoric systems undergoes this type of process. The

fluorescence of the arene is quenched in these systems but the indications are that the ester and amino groups contribute significantly to this effect.



(35)



(36)

In conclusion, the photoaddition reactions of benzene continue to provide fruitful and interesting areas of photochemical research, ortho and meta intermolecular cycloadditions of ethylenes to benzene and its simple derivatives is a general process. The relative efficiencies and preferred modes of reaction for particular systems are largely predictable so that the processes can be considered as realistic synthetic routes to bicyclo[4.2.0]octane and tricyclo[3.3.0.0^{2,8}]octane systems. The ortho cycloaddition process involves a measure of charge-transfer to or from the ethylene at some stage in the reaction pathway whereas to rationalise the orientational and regio selectivities of the meta reaction for the various systems studied, two mechanistic pathways have to be considered. Positions and modes of intramolecular reaction between the chromophores of non-conjugated phenyl vinyl bichromophoric systems are understandable in terms of favoured molecular conformations leading to preferred orientations of the addends. Our work in this area is on-going but studies suggest that the intramolecular process may arise from an excited complex although as yet emission from such a species has not been observed and it may well be that low efficiency 1,3-intramolecular cycloadditions occur via prior arene rearrangement followed by vinyl addition.

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