The Photo-cycloaddition of Enol Ethers to Benzene

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The photo-reactions of benzene with ethyl vinyl ether, n-butyl vinyl ether, 1,1-dimethoxyethylene, 2,3-dihydro-pyran, 2,3-dihydrofuran, 2,3-dihydro-1,4-dioxin, and 1,3-dioxole are described. The *meta*-photo-cycloaddition of ethyl vinyl ether and n-butyl vinyl ether to benzene shows little selectivity, and regio- and stereo-isomers are isolated. *ortho*-Cycloaddition is observed from all systems but only with 2,3-dihydrofuran as addend are both stereoisomers of the adduct formed, and although the *exo*-isomer is very photolabile, the *endo*-product is essentially stable under its conditions of formation. The *ortho*-cycloaddition of 1,1-dimethoxyethylene to benzene provides the first step in a convenient synthesis of cyclo-octatrienone. Contrary to previous proposals there is little correlation between the stereochemistry of the *ortho*-cycloaddition and preferred orientation of the addends in the ground state. The relationship between the relative efficiency of the two addition modes and ionisation potential of the ethylene is discussed.

THE formation of *ortho*-, *meta*-, and less commonly *para*-cycloadducts (1), (2), and (3) † respectively from the 254-nm irradiation of benzene and its simple derivatives in the presence of various ethylenes has been known for several years,[2] and yet the factors which can affect the relative efficiencies of the processes have not been fully elucidated. From a preliminary survey [3] of the photo-

(1)   (2)   (3)

additions of a variety of ethylenes to benzene, it has been proposed that the *ortho*-process 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 and proceeds from S_1 benzene.[2,4,5] Thus the *ortho*-process was found to be favoured in systems in which the electron-donor properties of the addends, as measured by ionisation potential, were appreciably different, and whereas this mode was favoured in polar solvents, the *meta*-reaction has been reported to be largely unaffected by change in solvent.[3,6,7] The proposals are consistent with deductions from orbital-symmetry analysis of these systems.[2,4,8] Vinylene carbonate and benzene, however, have a relatively large difference in ionisation potential and yet yield *meta*-cycloadducts,[9] and the ratio of *ortho* to *meta* cyclo-adducts from 1,3-dioxole and benzene [10] is less than may have been predicted from the preliminary survey.[3] The relationship between ethylene ionisation potential and the relative efficiency of the cycloaddition modes is further discussed along with the present results.

We have recently described in detail the photo-addition reactions of ethylenic hydrocarbons to benzene, which give mainly *meta*-cycloadducts.[6] In attempts to obtain a better understanding of the role of electron donor–acceptor properties of the addends in the *ortho*

and *meta* processes, and to determine the effect of the structure of ethylenes of similar ionisation potential on modes of photo-cycloaddition, we have studied the photo-reactions of benzene with several acyclic and cyclic enol ethers. As it transpired the structural features of the ethylene were found to be a dominant factor in affecting the selectivity of modes of reaction and for the first time lack of stereospecificity of *ortho*-cycloaddition of an electron-rich ethylene to S_1 benzene has been observed.
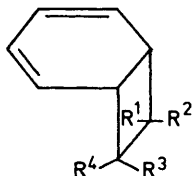
RESULTS

Details of the irradiation conditions and spectroscopic features of the adducts are given in the Experimental section. Preparative experiments generally involved undiluted solutions of the addends but in some systems, the proportions and amounts of the adducts were dependent upon the relative concentrations of the addends, the nature of the diluent and the time of irradiation.

Photoaddition of Acyclic Enol Ethers.—In a preliminary communication it has been reported that 254-nm irradiation of ethyl vinyl ether and benzene yields *ortho* and *meta* cycloadducts with respective quantum yields of 0.2 and 0.06, but stereochemical and, in the latter type of product, regiochemical assignments were not described.[3] We have, however, recently reported that only one *ortho*-cycloadduct is formed from this system and by its conversion to the Diels–Alder adduct (4) and the unambiguous synthesis of this we have shown that the ethoxy-group is *exo* in the original 1 : 1 *ortho*-cycloadduct.[11]
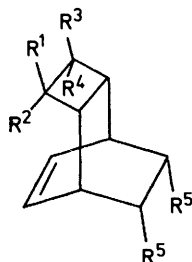
The 254-nm irradiation of equivolume mixtures of ethyl vinyl ether and benzene led to the formation of several 1 : 1 adducts (m.s./g.l.c. $M^+ = 150$), the ratios of which were time variant since the *ortho*-cycloadduct (5) reaches a photo-stationary state whereas linear build up of the *meta*-products continues for an appreciably longer time. Removal of (5), which co-eluted on g.l.c. with the longest retention time *meta*-adduct, as the 1 : 1 : 1 adduct (4), gave the *meta*-cycloadduct mixture which was separated into three components (ratio *ca.* 2.2 : 1.8 : 1, increasing retention time on Apiezon L columns). These fractions were separated by preparative g.l.c. with each of >95% purity. The shortest retention time adduct is assigned the *endo*-7-ethoxy-*meta*-cycloadduct structure (6) on the basis of its n.m.r. spectrum (Experimental section) and the effect on this of successive additions of a europium shift reagent. Consistent with this assignment, this adduct was also thermally the most

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† This system of nomenclature for adducts which were earlier referred to as 1,2-, 1,3-, and 1,4-cycloadducts follows that recently adopted to avoid ambiguity in describing the cyclo-additions of substituted benzenes.[1]

stable of the *meta*-products, since the substituted 7-*endo*-position prevents the facile [1,5] sigmatropic shift occurring to give the bicyclo[3.3.0]octa-2,7-diene isomer.[12] The n.m.r. spectrum of the component of intermediate abundance indicated, from the two sets of methyl resonances, the

is assigned the *exo*-6-ethoxy-structure (8). Detailed structural information concerning the minor isomer of this component could not be obtained, but as the *endo*-6-ethoxy-structure (9) is deduced from the n.m.r. spectrum for the product of longest retention time, it is proposed that the

(5) R^2 = OEt, R^1 = R^3 = R^4 = H
(15) R^1 = R^2 = OMe, R^3 = R^4 = H
(17) R^2—R^3 = —O—[CH$_2$]$_3$—, R^1 = R^4 = H
(26) R^2—R^3 = —O—[CH$_2$]$_2$—, R^1 = R^4 = H
(27) R^1—R^4 = —O—[CH$_2$]$_2$—, R^2 = R^3 = H
(29) R^2—R^3 = —O—[CH$_2$]$_2$—O—, R^1 = R^4 = H
(33) R^2—R^3 = —O—CH$_2$—O—, R^1 = R^4 = H

(6) R^3 = OEt, R^1 = R^2 = R^4 = H
(8) R^1 = OEt, R^2 = R^3 = R^4 = H
(9) R^2 = OEt, R^1 = R^3 = R^4 = H
(10) R^4 = OEt, R^1 = R^2 = R^3 = H
(12) R^3 = OBu^n, R^1 = R^2 = R^4 = H
(13) R^1 = OBu^n, R^2 = R^3 = R^4 = H
(14) R^2 = OBu^n, R^1 = R^3 = R^4 = H
(19) R^1—R^4 or R^2—R^3 = —O—[CH$_2$]$_3$—
(32) R^2—R^3 = —O—CH$_2$—O—, R^1 = R^4 = H
(34) R^1—R^4 = —O—CH$_2$—O—, R^2 = R^3 = H
(35) R^1 = R^2 = H, R^3 = R^4 = Me
(36) R^1 = R^2 = Me, R^3 = R^4 = H
(37) R^4 = Me, R^1 = R^2 = R^3 = H
(38) R^3 = Me, R^1 = R^2 = R^4 = H

(4) R^1 = OEt, R^2 = R^3 = R^4 = H, R^5—R^5 = CO—N(Ph)—CO
(16) R^1 = R^2 = OMe, R^3 = R^4 = H, R^5—R^5 = CO—O—CO
(18) R^1—R^3 = —O—[CH$_2$]$_3$—, R^2 = R^4 = H, R^5—R^5 = CO—N(Ph)—CO
(24) R^1—R^3 or R^2—R^4 = —O—[CH$_2$]$_2$—, R^5—R^5 = CO—N(Ph)—CO
(25) R^1—R^3 = —O—[CH$_2$]$_2$—, R^2 = R^4 = H, R^5—R^5 = CO—N(Ph)—CO
(28) R^2—R^4 = —O—[CH$_2$]$_2$—, R^1 = R^3 = H, R^5—R^5 = CO—N(Ph)—CO

presence of two products in a ratio of *ca.* 5.7 : 1. Since the mass spectrum of this component was consistent with a 1 : 1 adduct and integration of the n.m.r. spectrum was 2 vinyl
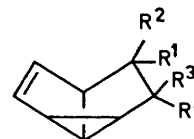
minor non-separated product is the fourth possible *meta*-cycloadduct (10) having the ethoxy-group in the *exo*-7-position. At 250 °C in the injection block of a g.l.c. the *meta*-cycloadducts (8), (9), and (10) gave a mixture of isomers which by analogy with related systems [6,12b,14] are assumed to be the three ethoxy-derivatives (11). Thus

(7)

protons to 12 others, it is deduced that two *meta*-adduct isomers are present.* These isomers could not be separated chromatographically, but from the n.m.r. spectrum and the effect of a europium shift reagent on this, the major isomer
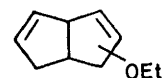

(11)

irradiation of ethyl vinyl ether and benzene yields regio- and stereo-isomers of the *meta*-cycloadduct, but only the *exo-ortho*-cycloadduct. A redetermination of the quantum yields for adduct formation gave values of 0.3, 0.075, 0.05, 0.03, and 0.008 (estimated) for (5), (6), (8), (9), and (10) respectively.

Irradiation of benzene in the presence of n-butyl vinyl

* The presence of a 1 : 1 adduct of structure (7) in this mixture was discounted both from the characteristic *meta*-cycloadduct n.m.r. spectrum, and also because (7) would be a secondary photo-adduct of (5):[13] no evidence was obtained for an increase in the concentration of this fraction with relative decrease in that of (5).

ether gave broadly similar results to those described above for the ethyl compound including the coincident elution of the *ortho*-cycloadduct with one of the *meta*-isomers. The ratio of products was again affected by the photo-lability of the *ortho*-cycloadduct, but the ratio of *ortho* to *meta* cyclo-addition rates was approximately 2.7 : 1. The *ortho*-cyclo-adduct has exclusively *exo*-stereochemistry.[11] The *meta*-cycloadducts were separated by preparative g.l.c. and from their n.m.r. spectra, and comparison with those from ethyl vinyl ether and benzene, we deduce that these products, formed in a ratio of 1.25 : 1.1 : 1.0, are the *endo*-7-, *exo*-6-, and *endo*-6-n-butoxy-isomers (12), (13), and (14), respectively. In this system, the *exo*-7-n-butoxy-*meta*-cycloadduct isomer was not detected. A preliminary study of t-butyl vinyl ether and benzene gave very similar results to those of the n-butyl compound, but the *ortho*-cycloadduct was separated chromatographically from the *meta*-isomers which had an internal ratio of *ca.* 1 : 1 : 0.5 for the analogous products to (12), (13), and (14), respectively: again the *exo*-7-isomer was not detected.

In view of the reported lack of reaction between *cis*-dimethoxyethylene and the low efficiency of both the *ortho* and *meta* cycloadditions of the *trans*-isomer (quantum yields of 0.04 and 0.03 respectively) [3] it was of importance to examine the structural features responsible for these observations, and thus to study the photo-process of 1,1-dimethoxyethylene and of other 1,2-ethenyl diethers with benzene.

Irradiation of an equivolume mixture of benzene and 1,1-dimethoxyethylene led to the rapid formation of a 1 : 1 adduct (M^+ 166) and the slow appearance of a yellow colour-ation. Distillation of the yellow oil after removal of the solvents gave a colourless oil (b.p. 60—75 °C at 0.05 mmHg) as the major fraction, and a minor amount of a yellow oil (b.p. 80—90 °C at 0.05 mmHg). The former fraction com-prised only one 1 : 1 adduct, while the latter contained minor amounts (<10%) of other 1 : 1 adducts, which, because of the low quantities obtainable, were not further investigated. Spectroscopic properties of the colourless distillate (Experimental section) were wholly consistent with the assignment of the *ortho*-cycloadduct (15) to this product. The adduct reacted quantitatively with dieno-philes, and with maleic anhydride gave the 1 : 1 : 1 adduct (M^+ 264) (16) (m.p. 104—106 °C). Trace amounts of acid added to a methanol solution of (15) gave high yields of a compound which was identified as cyclo-octatrienone from its spectroscopic properties. It is in complete agreement with the literature that the *ortho*-cycloadduct of benzene and 1,1-dimethoxyethylene exists in the bicyclic form whereas the derived ketone is monocyclic.[15] The con-venience of this photoaddition and the yield from acid treatment of (15) render the process an attractive route, compared to others available,[16] for the synthesis of cyclo-octatrienones.[17]

Photo-addition of Cyclic Ethenyl Mono- and Di-ethers to Benzene.—2,3-Dihydropyran. Irradiation of equimolar mix-tures of 2,3-dihydropyran and benzene led to the rapid formation of a 1 : 1 adduct (M^+ 162) which from spectro-scopic properties and reaction with N-phenylmaleimide has been assigned the *ortho*-cycloadduct structure (17) with exclusively *exo*-stereochemistry.[11] The stereochemistry was assigned on the basis of the effect on the proton re-sonance positions by successive additions of a europium shift reagent and the triplet appearance of the resonance of the ethenyl protons in the 1 : 1 : 1 N-phenylmaleimide

adduct (18). The *endo*-stereoisomer of (18) would have non-equivalent ethenyl protons and the resonance pattern would be more complex, as in the case of the maleic anhydride adduct (16) from 1,1-dimethoxyethylene and benzene, and one of the stereoisomers of the N-phenylmaleimide adduct of the 2,3-dihydropyran–benzene *ortho*-cycloadduct mixture (see later). As well as (17) four further 1 : 1 adducts were detected at longer retention time (Carbowax 20 M) but their combined proportion was always <5% of the total yield from preparative irradiations. On one occasion a small sample of the mixture of minor components was obtained by preparative g.l.c. and from the n.m.r. spectrum, par-ticularly the ethenyl proton resonances (characteristic *meta*-adduct multiplet centred at δ 5.5 and *para*-adduct double doublet centred at δ 6.3) this fraction is considered to consist of both *meta*-cycloadducts (19) and the *para*-cycloadduct (20). The quantum yield for formation of (17) in iso-octane was 0.7 and in acetonitrile 0.78, whereas those of the minor components appeared not to be influenced by change in solvent and had a combined value of <0.01. Irra-diation of this system in the presence of cyclopropyl bro-mide [18] under conditions such that 90% of the radiation was


(20) $R^1-R^2 = -[CH_2]_3-$

(31) $R^1-R^2 = -CH_2-O-$
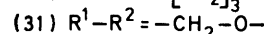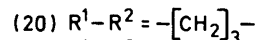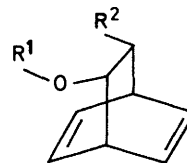
absorbed by benzene led to a 50% reduction in the rate of adduct formation: benzene fluorescence was also found to be quenched ($k_q = 3.82 \times 10^8$ l mol^{-1} s^{-1}) by cyclopropyl bromide. These data are simply interpreted as enhanced intersystem crossing of S_1 benzene and the necessary in-volvement of the S_1 state in formation of the *ortho*-cyclo-adduct (17). This state has been shown to be involved in the *meta*-cycloaddition process [5] and has also previously been implicated in the *ortho* and *para* reactions.[19]

The high efficiency of formation of (17) suggests that this could be a synthetically useful reaction, but irradiation (254 nm) of the *ortho*-cycloadduct in both iso-octane and benzene led to its rapid disappearance, so chemical yields of (17) are disappointing. The rate of disappearance of (17) in benzene solution was approximately 1.5 times that in iso-octane which is interpreted simply as the adduct undergoing a T_1 benzene-sensitised process. From neither reaction was evidence obtained for the formation of starting materials or the presence of the expected cyclobutane ring-opened isomer (21); [20] instead amounts of polymeric materials were deposited on the cell walls. In contrast, at g.l.c. injection block temperatures of 350 °C compound (17) was efficiently converted into an isomer which, from spectroscopic analysis and the effects of a europium shift reagent on the n.m.r. spectrum, is assigned structure (22). Formation of (22) is suggested to arise by homolysis of the C(1')–C(2) bond to give the biradical (23), which yields (22) by processes of [1,5] and [1,3] sigmatropic shifts. Specifically no 3-phenyltetrahydropyran was detected from the pyrolysis, although the analogous product was isolated by a thermal procedure from the *ortho*-cycloadduct of benzene and 2,3-dihydro-1,4-dioxin (see below).

2,3-Dihydrofuran. In contrast with the high selectivity of mode of reaction and stereospecificity of the *ortho*-cycloaddition of 2,3-dihydropyran and benzene, the irradiation of 2,3-dihydrofuran in benzene led to the formation of a complex mixture of products. Five 1 : 1 adducts (m.s./g.l.c. M^+ 148) were resolved by g.l.c. but their ratios were very dependent on reaction time and reactant concentration. The initial ratio of adducts in cyclohexane solution was *ca.* 0.5 : 5 : 50 : 30 : 0.5 (order of increasing retention time on Carbowax 20 M) but this rapidly changed with time to a ratio of 0.5 : 5 : 50 : 4 : 0.5. From preparative experiments involving equivolume mixtures of the reactants, although the initial relative yield of the fourth component was approximately that in the presence of a diluent, the photo-stationary state was rapidly reached and in practice the best ratio obtained of the initially major products in a distilled adduct mixture was 6 : 1. Both these 1 : 1 adducts
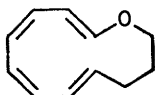
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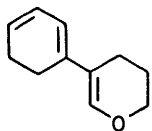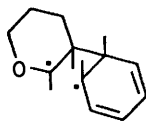
(22)   (23)

reacted readily with dienophiles and hence are deduced to be *ortho*-cycloadducts. The isomer of lower abundance reacted slightly more rapidly than the other adduct with *N*-phenylmaleimide (monitored by g.l.c.) and the resulting product was less soluble than that from the major isomer, thus separation of the 1 : 1 : 1 Diels–Alder adducts (M^+ 321) could be achieved. Structure (24) is assigned to the 1 : 1 : 1 adducts on the basis of spectroscopic analysis, elemental analysis, their mode of formation, and comparison with other systems.[11] The minor 1 : 1 : 1 adduct (m.p. 240—242 °C) was in general less soluble in all solvents than the major isomer (m.p. 224—225 °C) and their i.r. and n.m.r. spectra differed in detail. In particular the ethenyl protons of the minor isomer resonated as a triplet (J 4 Hz) centred at δ 6.4 and this feature is very similar to that in the *exo* 1 : 1 : 1 adduct (17) from 2,3-dihydropyran, whereas these protons in the major isomer appeared as two AB quartets with double doublets superimposed. These latter resonances were centred at δ 6.1 and 6.34 with J 7.75, 6.5, and 1.5 Hz. From these features we assign the *exo-endo*-structure (25) to the minor 1 : 1 : 1 adduct and hence (26) to the 1 : 1 *ortho*-photo-adduct of 2,3-dihydrofuran and benzene which is photo-labile, and the *endo*-structures (27) and (28) to the photo-stable major *ortho*-cycloadduct and the 1 : 1 : 1 Diels–Alder product of this, respectively.

This is a surprising result in view of those noted with very similar systems, in which *exo*-adducts are formed exclusively, and although these isomers are photo-labile to some extent, unlike the present *exo-ortho*-cycloadduct compound (26), can be easily obtained from preparative irradiations. Prolonged irradiation of the 2,3-dihydro-furan–benzene system allowed the preparation of gram quantities of the *endo-ortho*-cycloadduct to be obtained.

The spectra of this sample were wholly consistent with the assignment and this was substantiated by the effects of europium on the n.m.r. spectrum, when it was observed that the resonance of one of the ethenyl protons moved more rapidly than the others. This feature was not observed with the *exo-ortho*-cycloadduct (17), and is simply attributed to the proximity of the europium atom in space to one proton on the diene system in the *endo*-isomer (27). The reaction mixture, after treatment with *N*-phenyl-maleimide, had four 1 : 1 adducts in an approximate ratio of 1 : 10 : 10 : 1. The n.m.r. spectrum of this mixture showed that all the *ortho*-cycloadducts had been removed; thus the major *ortho*-cycloadduct is deduced to co-elute with a further 1 : 1 adduct. From this spectrum it was also deduced that at least the two major 1 : 1 adducts remaining after the Diels–Alder reaction were a mixture of regio- and stereo-isomers of the *meta*-cycloadducts. Since the main objective for this system of the determination of the ratio of modes of reaction had been achieved, and because of the minor amounts of the *meta*-isomer mixture obtained, further separation was not attempted.

Thus the ratio of efficiency of *ortho* to *meta* cycloaddition of 2,3-dihydrofuran to benzene is calculated to be 7.5 : 1, respectively.

In view of these contrasting results with five- and six-membered ring mono-ethers of similar ionisation potential, it was now considered of importance to examine the corresponding diethers: these latter systems are also of interest, as mentioned above, in view of the results with 1,2-di-methoxyethylenes.[3]

2,3-Dihydro-1,4-dioxin. 2,3-Dihydro-1,4-dioxin was prepared in ethereal solution [21] and was used as such in preparative irradiations with benzene: a small quantity was isolated pure for spectroscopic studies and to demonstrate that diethyl ether diluent had no detectable effect on product formation. Irradiation of the 2,3-dihydro-1,4-dioxin–ben-zene system gave three 1 : 1 adducts (m.s./g.l.c. M^+ 164), but the one of intermediate retention time constituted >98% of the adduct mixture: the minor products were not further investigated. The major product has been shown to be the *exo-ortho*-cycloadduct (29) by *X*-ray crystallographic analysis of the 1 : 1 : 1 adduct formed with *p*-bromo-*N*-phenyl-maleimide.[22] Attempts to purify (29) directly from the irradiation by preparative g.l.c. gave a fraction which contained 90% of an isomer. Residual (29) was removed by treatment with a dienophile and the resultant isomer characterised as 2-phenyl-1,4-dioxan by comparison of its spectroscopic properties with those in the literature.[23] No part of the preparative chromatograph was at a temperature greater than 200 °C, so the isomerisation is facile. Controlled pyrolysis of (29), however, at temperatures up to 350 °C, resulted in the formation of a further isomer and no evidence for 2-phenyl-1,4-dioxan was obtained. From spectroscopic analysis, the ' new ' isomer was assigned structure (30). Formation of (30) from (29) is not unexpected but it is not evident why (29) should only yield
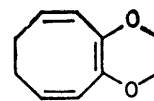
(30)

2-phenyl-1,4-dioxan on attempted purification by g.l.c. unless the transformation was surface-catalysed in some part

of the instrument. Not surprisingly 2-phenyl-1,4-dioxan did not yield (30) on heating up to 500 °C and (30) also proved to be essentially stable up to 350 °C, above which temperature several products, not including 2-phenyl-1,4-dioxan, were formed. These thermal results contrast interestingly with those observed with the *exo*-2,3-di-hydropyran–benzene *ortho*-cycloadduct (17).

1,3-*Dioxoles.* Our studies of the photo-reactions of 1,3-dioxole and 2-methyl-1,3-dioxole with benzene were at a comparatively early stage when detailed studies of other workers on these systems were communicated to us.* We terminated our investigations as soon as we were assured that the results were completely in accord with those now published by Scharf and his co-workers.[10] Thus from the 1,3-dioxole–benzene system four 1 : 1 adducts are formed in the approximate ratio at the photo-stationery state of 1 : 62 : 20 : 15; these are respectively assigned the *para*-structure (31), the *endo-meta*-structure (32), the *exo-ortho*-structure (33), and the *exo-meta*-structure (34).

The ratio of *ortho* to *meta* cycloaddition from quantum yield values † is *ca.* 1 : 2, respectively. Similarly the 2-methyl-1,3-dioxole–benzene system showed little selectivity and gave all three types of cycloaddition, but in this case the efficiency of *ortho*-cycloaddition was approximately 3.5 times that of the corresponding *meta*-process, and that for the *para*-cycloaddition was very low indeed.
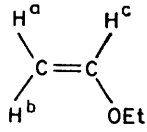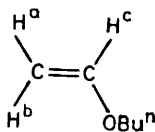
DISCUSSION

It is evident from the present results that the photocycloaddition of ethenyl ethers to benzene in the liquid phase is a general process, but that the relative efficiency of the modes of reaction varies markedly with the particular addend. It has been previously reported that *meta*-cycloaddition arises from the S_1 state of the arene [5] and it was considered likely that this is also the excited state responsible for *ortho* and *para* processes, since the relative initial yields of the benzene–*cis*-but-2-ene adduct were found to be constant over a wide range of reactant concentrations and proportions.[19] By use of a heavy-atom solvent we have confirmed the involvement of the arene S_1 state in the *ortho*-cycloaddition of an ethylene to benzene. The *ortho*-cycloaddition is non-allowed as a concerted process from S_1 benzene [8] but this can be overcome by the proposal that the reaction involves an excited state complex in which mixing of states results in the relaxation of orbital symmetry restrictions.[4,19] This matter has been previously discussed,[2] and is consistent with the proposal [3] that the *ortho*-cycloaddition would involve an element of charge transfer to or from the ethylene: consistent with this, the quantum yield for formation of (17) is increased by 10% in the presence of polar solvents compared to that in cyclohexane.

It has been reported from a study of several ethylene–arene systems that the *meta*-photo-cycloaddition results in the formation of both *exo* and *endo* isomers, but that the latter stereoisomer always predominates and in some cases may be the exclusive isomer.[2,26-28] From stereochemical elucidations of the *ortho*-cycloadducts of *cis*-

but-2-ene,[19] *cis*-cyclo-octene,[29] maleic anhydride,[30] and maleimide,[31] it appeared that electron-donor ethylenes would yield *endo*-stereoisomers whereas with electron-acceptor ethylenes, the *exo*-product would be formed exclusively.[3] In these cases, the stereochemistry of the *ortho*-cycloadducts was a remarkable reflection of the preferred orientation of the addends in the ground state as deduced from n.m.r. spectroscopic studies.[32] We have examined the predictive value of this concept with other dienophilic ethylenes [11] and in the present study with electron-rich ethylenes, and would now emphasise that with two exceptions (refs. 19 and 29) *exo*-stereoisomers are formed in all cases but that in some systems the *ortho*-cycloaddition process lacks selectivity and has little relation to the orientation of the addends in the ground state. Thus although acrylonitrile yields exclusively the *exo-ortho*-cycloadduct, both *exo* and *endo*

^{1}H N.m.r. spectroscopic measurements of the ethenyl ethers in CCl_4 and C_6D_6 at 33 °C

Compound	Shift in C_6D_6 *cf.* CCl_4 *	
H^a \ / H^c C=C / \ H^b OEt	H^a 4 Hz df H^b 6 Hz df H^c 4 Hz df	methylene 16 Hz uf methyl 12 Hz uf
H^a \ / H^c C=C / \ H^b OBu^n	H^a 4 Hz df H^b 8 Hz df H^c 4 Hz df	methylenes 10 Hz uf methyl 12 Hz uf
2,3-Dihydrofuran	2-ethenyl no change 3-ethenyl 8 Hz uf	4-methylene 22 Hz uf 5-methylene 14 Hz uf
2,3-Dihydropyran	2-ethenyl 10 Hz df 3-ethenyl no change	4- and 5-methylenes 18 Hz uf 6-methylene 11 Hz uf
1,3-Dioxole †	ethenyl 20 Hz uf	methylene 18 Hz uf
2-Methyl-1,3-dioxole †	ethenyl 13 Hz uf	methine 4 Hz uf methyl 11 Hz uf
2,3-Dihydro-1,4-dioxin †	ethenyl 3 Hz uf	methylenes 25 Hz uf

* df = Downfield, uf = upfield. † See also ref. 25 for similar values for these compounds.

stereoisomers are formed from the corresponding reaction with methyl vinyl ketone,[11] methyl acrylate,[11] methyl methacrylate,[11] and methacrylonitrile.[34] With the exception of 2,3-dihydrofuran, the *ortho*-cycloadducts from acyclic and cyclic ethenyl ethers have *exo*-stereochemistry exclusively, and yet on the basis of ^{1}H n.m.r. spectroscopic studies, it could be deduced that an *endo*-relationship of the addends in the ground state would be preferred: the ^{1}H n.m.r. data for the present systems are summarised in the Table. Only in the case of 2,2-dimethyl-1,3-dioxole is there a clear indication for an *exo*-orientation in the ground state.[25] Hence it must be

† The *para*-cycloadduct (31) arises from a secondary photoreaction of (33). Quantum yields for (32), (33), and (34) are respectively 0.31, 0.21, and 0.07.[25]

concluded that ground-state orientations of the addends as deduced by n.m.r. spectroscopy, have little or no influence on the stereochemistry of the *ortho*-cyclo-addition process.

In view of the previous studies with ethylene–benzene systems,[2] the most unexpected result from the present investigation is the formation of both *exo*- and *endo*-*ortho*-cycloadducts from irradiation of 2,3-dihydrofuran and benzene, particularly since the addition of 2,3-dihydropyran is stereospecifically *exo*. Initially both stereoisomers are formed in comparable concentrations but the *exo*-isomer is clearly and surprisingly very photo-labile, whereas the *endo*-product appears to be essentially stable under the conditions of its formation. The *exo-ortho*-cycloadducts obtained from the other systems do have varying photo-labilities and with the vinyl ethers prolonged irradiation gave essentially only the *meta*-products, but only with 2,3-dihydrofuran has the lack of specificity in the *ortho*-cycloaddition been observed and the formation of the *endo*-isomer proved. There appears to be no ready explanation for such different reactivity and the photo-lability of one isomer or the stability of the other.

The predictive usefulness of the concept of a relationship between the difference in ionisation potentials of the addends (ΔI.P.) and the preferred mode of photo-cycloaddition of ethylenes to benzene [3] requires some discussion. We have noted elsewhere [6] that it may be too restrictive to quote exact values of ethylene ionisation potentials (*i.e.* ionisation potential <8.65 and >9.6 eV [3]) below and above which the *ortho*-cycloaddition will be more efficient than the corresponding *meta*-process. Even so, there have been a number of examples of cyclo-addition reported since the original proposal which support the predictive value of the ionisation potential-preferred mode of addition relationship.[2] However, it must be recognised that there are *ortho* and *meta* cyclo-additions of ethylenes to benzenes, the relative efficiencies of which fall outside those predicted from ionisation potentials, and it may be more meaningful to relate the relative efficiencies of the two processes with ΔI.P. only within a series of structurally very similar ethylenes. For example there is some degree of correlation between the ΔI.P. values of ethylene and the methylethylenes and benzene and their relative efficiencies of *ortho* and *meta* cycloaddition measured at low conversions and under comparable conditions,[3,6,19,34] (*i.e.* as ΔI.P. increases so does the ratio of *ortho* to *meta* addition efficiencies). In the present systems too there is a gradation of relative efficiencies with ionisation potential. Thus with 1,3-dioxole (I.P. 8.56 eV) the relative efficiency of the *ortho* to the *meta* cycloaddition process is 1 : 1.8 and this changes to 1 : 1 for the reactions with 2-methyl-1,3-dioxole (I.P. 8.36 eV) and to 3.5 : 1 for 2,2-dimethyl-1,3-dioxole (I.P. 7.92 eV).[25] This trend is also evident with ethyl vinyl ether and 1,1-dimethoxyethylene but surprisingly, in the cases of 1,3-dioxole and 2,3-dihydro-1,4-dioxin, and 2,3-dihydrofuran and 2,3-dihydropyran, in which the ionisation potentials of the ethylene within

the pairs are very similar, there is seemingly no such relationship. Indeed the only obvious common feature in these systems is that the five-membered ring ethers yield both *ortho* and *meta* cycloadducts whereas the reactions of the six-membered ring compounds are far more selective giving almost exclusively *ortho*-cyclo-adducts. The features of the ethylenes which control the reaction efficiencies are clearly very subtle and may involve minor steric interactions of the addends. Even so, in view of the present results with 2,3-dihydro-1,4-dioxin there appears to be no ready explanation for the failure of *cis*-dimethoxyethylene to undergo photo-addition to benzene.

It is interesting to compare the reactivities of the five- and six-membered cyclic ethenyl mono- and di-ethers towards photo-excited benzene with those of cyclo-pentene [6,35] and cyclohexene.[6] Cyclopentene yields *meta*-cycloadducts with only traces of the ethylene dimers whereas with cyclohexene, the efficiency of the photo-reaction with benzene is very low and cyclobutane dimers formed by T_1 benzene sensitisation constitute a significant proportion, dependent upon the reactant concentration, of the product mixture.[6] Neither 2,3-dihydropyran nor 2,3-dihydro-1,4-dioxin behave in this manner but in view of the results with cyclohexene, 3,4-dihydropyran, not surprisingly, shows a low reactivity towards S_1 benzene and ethylene dimers are among the small yields of photo-products.[36] Of the vinyl alkyl ethers studied in the present work, only n-butyl vinyl ether gave evidence for the formation of cyclobutane ethylene dimers, and these in low yield.

Finally the two further points of regio- and stereo-selectivities in *meta*-cycloadditions of ethylenes to benzene and the involvement of exciplexes in the present photo-cycloadditions require some comment. Published evidence concerning regioselectivity of the addition is sparse and whereas there is little regioselectivity in the addition of 2-methylpropene to benzene [5 : 4 ratio of (35) to (36)],[6] in contrast, the two *meta*-adducts from propene and benzene ' are most likely ' the 7-*exo*- and 7-*endo*-isomers (37) and (38),[34] rather than either of the 6-methyl isomers. One of the interests in the present study was to assess if a polar ethylene substituent would promote to any extent stereo- and/or regio-selectivity in the *meta*-cycloaddition but all four isomers from ethyl vinyl ether and benzene have been observed and the degree of selectivity in the addition is not remarkably high since the ratio of *exo*- to *endo*-isomers is *ca.* 1 : 1.8 (*cf* 1 : 4.44 for the corresponding addition of 1,3-dioxole [25]) and of the 6- to 7-substituted isomers is *ca.* 1 : 1. Intro-duction of a larger alkyl group to the ether (n-butyl, t-butyl) does change these ratios somewhat in that the *endo*-stereoisomers and 6-alkoxy-isomers become more favoured, but in general it appears that the alkoxy-substituent has little directing effect on the overall process.

The involvement or otherwise of exciplexes in the photo-addition of ethylenes to benzene and its derivatives has been discussed for several years.[6,26-28,37] Quenching

of the arene fluorescence by alkenes is reported to be very weak but the efficiency does increase with the electron-donor properties of the ethylene.[38] Not until very recently, however, has the emission from an ethylene-benzene exciplex been observed, and then only for ethenyl diethers at high reactant concentrations and in acetonitrile solvent: no emission was observed in cyclo-hexane.[25,39] In the case of the benzene–2,2-dimethyl-1,3-dioxole system, it has been shown that triethylamine quenches the exciplex emission at an almost identical rate to the *meta*-cycloadduct formation and hence it is reasonably considered very likely that the reaction proceeds *via* the fluorescent exciplex.[25] Under no conditions have we observed emission attributable to an exciplex from any of the mono-ethers in the present study, but quenching of the arene fluorescence does occur with varying efficiencies and it is certainly tempting to involve an exciplex in a mechanistic scheme.

However, more detailed physical studies are required on the present systems for meaningful discussion on this point, and it should be realised that there are *meta*-cycloadditions of ethylenes to benzene derivatives which are better understood in terms of a ' prefulvene ' mechanism[40] than by the involvement of a ' sandwich ' exciplex.[27,28]

EXPERIMENTAL

Irradiations were performed in base-washed quartz tubes of varying capacity. Hanovia 15-W low-pressure mercury-arc lamps were used throughout. The effect of solvents on the reactions was determined using 1.1M benzene and 3.5M of the ethylene and quantum yields were measured at the same concentrations using iso-octane as the diluent. Stirring or degassing the solutions had no measurable effect within the time limit of the quantitative experiments.

Irradiation of Ethyl Vinyl Ether and Benzene.—Benzene (75 ml) and freshly distilled ethyl vinyl ether (75 ml) were irradiated using two 15-W lamps for 36 h and gave, after removal of the reactants *in vacuo ca.* 2 g of a sweet-smelling oil (b.p. 50—60 °C at 1.0 mmHg). The *ortho*-cycloadduct (5) was isolated as the 1 : 1 : 1 *N*-phenylmaleimide adduct (4), details of which have been given elsewhere.[11] The *meta*-cycloadduct mixture was separated by preparative g.l.c. using Apiezon L as the liquid phase. The n.m.r. spectrum (100 MHz, C_6D_6) of (6), (8), and (9), the 7-*endo*-, 6-*exo*-, and 6-*endo*-ethoxy-derivatives of (2), respectively are as follows. Compound (6) δ 1.1 (3 H, t. Me), 1.4—2.2 (4 H, m), 2.36—2.65 (1 H, q, *J* 7 Hz), 2.75—2.95 (1 H, br t, *J* 7 Hz), 3.05—3.50 (2 H, q, *J* 7 Hz), 4.10—4.35 (1 H, br t, *J* 5 and 0.5), 5.38—5.50 (1 H, split dd, *J* 5.5, 2, and 0.5 Hz), and 5.64—5.78 (1 H, dd, *J* 5.5 and 2 Hz); (8) δ 1.1 (3 H, 2 × t, ratio *ca.* 5.7 : 1, Me), 1.6—1.95 (3 H and 1 H, m and dd, *J* 7 and 1.5 Hz), 2.6 (1 H, q, *J* 7 Hz), 3.05—3.30 (1 H and 2 H, m and q, *J* 7 Hz), 3.40—3.55 (1 H, dt, *J* 4 and 0.75 Hz), 5.18—5.32 (1 H, ddt, *J* 5.5, 2.5, and 0.75 Hz), and 5.40—5.52 (1 H, dd, *J* 5.5 and 1.5 Hz); (9) δ 1.05 (3 H, t, Me), 1.55—2.20 (4 H, and 1 H, m and q, *J* 7 Hz), 3.0—3.35 (1 H and 2 H, m and q, *J* 7 Hz), 3.76—4.04 (1 H, ddd, *J* 9, 8, and 5 Hz), and 5.56—5.80 (2 H, 2 × dd, *J* 5.5, 2.0, and 0.7 Hz). Corresponding n.m.r. spectra of the n-butyl compound were very similar to those above but with two further methylene proton resonances in the δ 1.3—1.6 region.

Spectra of the 1 : 1 : 1 *N*-phenylmaleimide derivative of the *ortho*-cycloadduct are given in ref. 11.

Irradiation of 1,1-Dimethoxyethylene and Benzene.—An equivolume solution (120 ml) of benzene and 1,1-dimethoxyethylene gave a crude yellow product (*ca.* 1.5 g) after a 24-h irradiation and removal of the starting materials (for recycling). The combined yield from four experiments was distilled (see text) and the colourless product had the following spectroscopic properties: $\lambda_{max.}$ (cyclohexane) 258 nm; $\nu_{max.}$ (Nujol) 3 050w, 3 030s, 2 980, 2 940s, 2 900, 2 830s, 1 640w, 1 580m, and multiple absorptions in the 1 190—1 158, 1 120—1 105, 1 080—1 060, and 1 050—1 030 cm^{-1} regions; and δ (60 MHz, CDCl$_3$) 2.2—2.4 (2 H, m), 2.6—2.9 (1 H, m), 3.2 (6 H, s), 3.65—3.75 (1 H, m), and 5.45—5.8 (4 H, m).

Maleic anhydride (0.2 g) was added to a solution of (15) (0.35 g) in diethyl ether (15 ml). The solution was refluxed for 2 h, cooled to 8 °C, and after 2 d the crystals of (16) (0.5 g) (*M*$^+$ 264), m.p. 104—105 °C, were filtered off; δ (60 MHz, CDCl$_3$) at 1.45—1.75 (1 H, dd, *J* 12.5 and 5 Hz), 1.8—2.2 (1 H, m), 2.3—2.5 (2 H, m), 3.0 (3 H, s), 3.1 (3 H, s), 3.0—3.25 (4 H, m), and 5.95—6.55 (2 H, quintet, *J* 8.5 and 6 Hz); $\nu_{max.}$ (Nujol) 1 770 cm^{-1}.

To a solution of (15) (0.7 g) in methanol (15 ml) concentrated hydrochloric acid (0.1 ml) was added with stirring and the mixture then refluxed for 30 min. The cooled solution was shaken with sodium hydrogencarbonate and extracted with diethyl ether, which yielded cyclo-octatrienone (*ca.* 0.5 g).

Irradiation of 2,3-Dihydropyran and Benzene.—The *ortho*-cycloadduct (17) (see ref. 11 for its spectroscopic properties) was pyrolysed under nitrogen at 350 °C for 30 s, which gave *ca.* 80% of the isomer (22) (*M*$^+$ 162). This isomer had $\lambda_{max.}$ (cyclohexane) 270 nm (ε 1 900 l mol^{-1} cm^{-1}); $\nu_{max.}$ (liquid film) 3 000m, 2 920s, 2 860s, 1 625s, 1 440s, 1 140s, and 750s cm^{-1}; δ (60 MHz, C$_6$D$_5$CD$_3$) 1.4—2.0 (4 H, m), 2.2—2.4 (4 H, m), 3.6—3.9 (2 H, m), and 5.6—6.0 (4 H, m): coupling of the first and third, and second and fourth resonances, was demonstrated.

Irradiation of 2,3-Dihydrofuran and Benzene.—As outlined in the text the relative proportions of the 1 : 1 adducts from this system varied with time. Prolonged irradiation (24 h) of an equivolume mixture (150 ml) of the addends gave *ca.* 1 g of distilled (100—108 °C at 0.05 mmHg) product which was >90% of (27); δ (100 MHz, CDCl$_3$) at 1.5—2.4 (2 H, m), 3.1—3.6 (2 H, m), 3.8—4.25 (2 H, m), 4.3—4.6 (1 H, m), 4.65—4.85 (1 H, m), and 5.2—5.9 (4 H, m); $\nu_{max.}$ (liquid film) 3 030s, 2 950s, 2 890s, 1 570w, 1 110m, 1 080s, and 715s cm^{-1}; $\lambda_{max.}$ (cyclohexane) 277 nm (ε 2 100 l mol^{-1} cm^{-1}).

Treatment of this sample (1.0 g) in diethyl ether (40 ml) with *N*-phenylmaleimide (1.2 g) gave, after 4 d at room temperature, the 1 : 1 : 1 adduct (28), m.p. 224—225 °C, *m/e* 321 (*M*$^+$) (1.85 g) (Found: C, 74.5; H, 6.1; N, 4.8. C$_{20}$H$_{19}$O$_3$N requires C, 74.75; H, 5.9; N, 4.36%); $\nu_{max.}$ (Nujol) 1 703s, 1 600w, 1 235m, 1 200s, 955m, 745m, 729m, 705m, and 690m cm^{-1}; δ (100 MHz CDCl$_3$) at 1.7—2.0 (2 H, m), 2.55—2.75 (2 H, m), 2.78—2.85 (2 H, m), 3.0—3.4 (3 H, m), 3.5—3.8 (1 H, q, *J* 8 Hz), 3.85—4.15 (1 H, br q, *J* 8 Hz), 4.4—4.6 (1 H, m), 6.0—6.2 (1 H, AB q + dd), 6.25—6.45 (1 H, AB q + dd), 7.05—7.3 (2 H, m), and 7.3—7.55 (3 H, m). A sample of the photo-adduct mixture (1 g) which had an estimated 6 : 1 ratio of (27) : (26) was treated with *N*-phenylmaleimide (1.2 g) in diethyl ether (40 ml) at room temperature. The crystals (0.2 g) which separated

in the first hour had m.p. 240—242 °C (with some decomp.), m/e 321 (M^+) (Found: C, 74.3; H, 6.2; N, 4.9. $C_{20}H_{19}NO_3$ requires C, 74.75; H, 5.9; N, 4.36%); $\nu_{max.}$ (Nujol) 1 713s, 1 600w, 1 228w, 1 175m, 1 055m, 730m, 710m, 695w, and 678w cm^{-1}; δ (100 MHz, CDCl$_3$) 1.55—1.85 (2 H, m), 1.9—2.15 (1 H, m), 2.25—2.55 (2 H, vbr m), 2.8—2.9 (2 H, m), 3.3—3.55 (2 H, vbr m), 3.7—4.25 (3 H, m), 6.3—6.5 (2 H, t, J 4 Hz), 7.1—7.3 (2 H, m), and 7.3—7.55 (3 H, m).

Irradiation of 2,3-Dihydro-1,4-dioxin with Benzene.—The *ortho*-cycloadduct (29) (see ref. 11 for its spectroscopic properties and ref. 22 for proof of stereochemistry) was subjected to preparative g.l.c. (Carbowax 20M liquid phase) which gave a fraction containing 90% of 2-phenyl-1,4-dioxan.[23] Pyrolysis of (29) at 350 °C for 10 s under nitrogen gave (30), m/e 164 (M^+); $\nu_{max.}$ (liquid film) 3 010m, 2 970m, 2 920s, 2 870s, 2 830m, 1 685w, 1 635s, 1 275m, 1 210s, 1 180s, 1 120m, 1 060m, 1 000m, 930m, 895m, 830w, 760m, and 730m cm^{-1}; $\lambda_{max.}$ (cyclohexane) 273 and 285 nm; δ (60 MHz, CDCl$_3$) 2.2—2.35 (4 H, m), 3.6 (4 H, s), 5.4—5.8 (2 H, db m, J 12 Hz + several smaller couplings), and 6.1 (2 H, d, J 12 Hz).

Irradiation of 1,3-Dioxole and 2-Methyl-1,3-dioxole with Benzene.—The substance of these experiments and the spectroscopic details of the adducts have been published by Scharf and his co-workers.[10,24,25] Our experiments and results differed from these in only minor insignificant details.

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