Photochemical Reactions of Benzene Derivatives with Electron-donor Ethylenes

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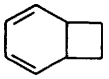
The photoreactions of ethyl vinyl ether with benzonitrile, toluene, and anisole are reported and compared with those involving benzene as the arene. As the difference in ionisation potential between the addends decreases, the *ortho*-cycloaddition reaction becomes less favoured and the *meta*-process predominates. Regio- and stereoisomers are formed in both photo-cycloaddition reactions. The *meta*-cycloadditions to toluene and anisole are exclusively 2,6- as are those of 2-methyl- and 2,3-dimethyl-but-2-ene to anisole. The effect of solvent on the *meta*-cycloaddition of anisole and ethyl vinyl ether has not been observed in any other system and suggests the involvement of a polar species in the reaction pathway.

IN recent years, the factors which influence the mode of photo-cycloaddition of ethylenes to benzene have received considerable attention.[1] It was proposed from a study of several systems that the ratio of the efficiency of the formation of the *ortho*- (1) and *meta*- (2) † cycloadducts from benzene could be predicted from a knowledge of the ionisation potential difference (ΔI.P.) between the addends.[2] In particular it was suggested that the former process would be favoured for ethylenes with ionisation potentials >9.6 or <8.65 eV, but for ethylenes with values similar to that of benzene, essentially only *meta*-cycloadducts would be formed. We have recently reported that the correlation of relative efficiency of addition modes with ethylene ionisation potential holds well in a series of ethylenes of very similar structure but that ethylenes of similar ionisation potentials having differing structural features can undergo the *ortho*- and *meta*-cycloadditions to benzene with markedly varying relative efficiencies.[3]



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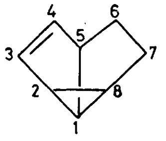


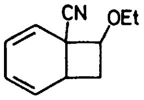
(2)

Previous studies into such aspects of these photoaddition reactions have involved one arene with ethylenes of differing ionisation potential and structure.[4-6] In order to assess the involvement of polar intermediates in these intriguing reactions, and the usefulness of the relative ionisation potentials of the addends in predicting preferred modes of photo-cycloaddition of ethylenes to arenes, we have studied in detail the photochemical reactions of benzonitrile (I.P. 10.02 eV), toluene (I.P. 8.82 eV), and anisole (I.P. 8.54 eV) with the electron-rich ethylene ethyl vinyl ether, and compared the results with those obtained with benzene (I.P. 9.24 eV) as the arene. As described below it was necessary, in order to complete this investigation, to study the photo-reactions of anisole with hydrocarbon ethylenes which have ionisation potentials similar to that of ethyl vinyl ether (*i.e.* 8.6 eV). The present paper also extends and amplifies the solvent effects in these systems which we outlined in a recent communication.[7]

RESULTS

Details of the irradiation conditions are described in the Experimental section. The effect of air or nitrogen on product formation was negligible under our reaction conditions and low-pressure mercury-arc lamps were used throughout the study. Undiluted solutions of the addends were used in preparative experiments, but in some systems amounts and ratios of adducts were dependent upon the nature of the diluent and period of irradiation.

Benzonitrile–Ethyl Vinyl Ether.—In 1963 Büchi and his coworkers reported that irradiation of benzonitrile and ethyl vinyl ether gave a ' 1 : 1 adduct which we believe to be 8-ethoxybicyclo[4.2.0]octa-2,4-diene-1-carbonitrile ' (3) but no structural details were given.[8] Recently Cantrell examined the photo-addition of several ethylenes, but not ethyl vinyl ether, to benzonitrile and reported that addends with ionisation potentials $\leqslant 8.5$ eV gave solely azetines (4) and 2-azabutadienes (5) by addition to the nitrile function, whereas bicyclo[4.2.0]octa-2,4-dienes (*ortho*-cycloadducts) were formed from ethylenes with ionisation potentials >8.8 eV.[9] Thus the former type of product was to be expected from ethyl vinyl ether.



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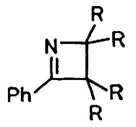

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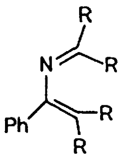

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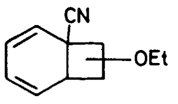

(6)

Irradiation of the benzonitrile–ethyl vinyl ether system in our laboratory gave, after distillation (80—95 °C at 0.05

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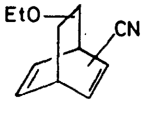
† *ortho*- and *meta*-Additions have previously been described as 1,2- and 1,3-additions, respectively, but the former terms are preferred here as they avoid ambiguities which would otherwise arise with these additions to the substituted benzenes described in the present paper.

mmHg), a pale yellow oil which darkened in air at room temperature over several days. The product is considered to be comprised mainly of regio- and stereo-isomers of ethoxybicyclo[4.2.0]octa-2,4-diene-1-carbonitrile (6) on the basis of the following evidence. G.l.c. analysis of the oil on packed columns (Carbowax 20M) revealed the presence of four major components with one constituting *ca.* 50% of the whole product mixture. Multiple mass scanning through the eluted components showed that all products were 1 : 1 adducts ($M^+ = 175$) of the starting materials but indicated the presence of two different types of structure. Thus in approximately 85% of the total mixture the base ion was of m/e 103 (benzonitrile) and this ready fragmentation to starting materials is indicative of *ortho*-cycloadducts,[10] whereas the remaining components had a base ion at m/e 119 and a relatively intense parent ion. Examination of reaction mixtures on a Squalane S.C.O.T. column revealed the presence of 11 components, four of which constituted *ca.* 80% of the whole mixture and which were removed from the chromatograph at high injection block temperature or by treatment of the sample with *N*-phenylmaleimide, properties consistent with a mixture of *ortho*-cycloadducts.[11] At least two of the minor components, which were essentially unaffected by added dienophile and were thermally very labile, could thus be *para*-cycloadducts (7) of benzonitrile and ethyl vinyl ether. The n.m.r. spectrum (see Experimental section) of freshly distilled samples of the adduct mixture was overall consistent with the bicyclo[4.2.0]octadiene structure (6) in that the ratio of ethenyl protons to the remainder was 4 : 9. This ratio increased slightly with the age of the sample and absorptions in the 290—330 nm region of the u.v. spectrum also appeared: these data are consistent with the formation of the tetraene (8) by thermal ring opening of the *ortho*-cycloadduct (6). The methyl resonance was clearly composed of several triplets indicating the presence of several isomers. Significantly, no resonance was observed at δ 7.3 which is the position at which the aryl protons of the azetine (4) and the 2-azabutadiene (5) resonate, so no significant addition of ethyl vinyl ether to the nitrile function had apparently occurred: this is a surprising result in view of those reported by Cantrell[9] with ethylenes of I.P. similar to that of ethyl vinyl ether and emphasises the point that ethylenes of similar I.P. but with different structural features may react in quite different ways.[3] Successive additions of a europium shift-reagent to the n.m.r. spectroscopic sample caused all the resonances to move downfield to some extent, but in particular this procedure split the methyl resonance into five overlapping but clearly discernable triplets with approximate integrals of 5 : 14 : 7 : 1 : 2 (low to high field) and thus confirmed the presence of several *ortho*-cycloadduct isomers in the mixture.



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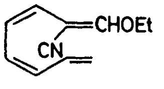
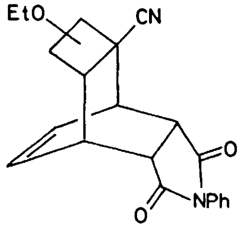


(8)

The adduct mixture reacted with *N*-phenylmaleimide in diethyl ether at room temperature over 6 d to give an approximately 80% yield of 1 : 1 : 1 adducts ($M^+ = 348$). Spectroscopic analysis of the crystalline product was consistent with a mixture of isomers of (9). In particular the multiplicity of the ethenyl proton resonance indicates the presence of both *exo*- and *endo*-stereochemistry of the ethoxy-group in (9) and therefore in (6).[11] The material after removal of (9) was largely polymeric. Attempts to reduce the reaction time of the Diels–Alder process and thereby obtain monomeric residual products which did not have a 1,3-diene moiety were unsuccessful; either polymeric materials were obtained, or the mixture was too heavily contaminated with (6) to allow meaningful spectral interpretation.

Thus the benzonitrile–ethyl vinyl ether system, which has the largest ΔI.P. between the addends, yields mainly regio- and stereo-isomers of the *ortho*-cycloadduct (6). No evidence was obtained for the formation of the corresponding *meta*-cycloadducts (10) or indeed addition of the ethylene to the nitrile function which had been rexpected, but *para*-cycloaddition may be a minor reaction pathway: this latter process could, however, be a secondary photoreaction of the *ortho*-cycloadducts (6) as is observed in the *para*-cycloaddition of 1,3-dioxoles to benzene.[3,12]

Toluene–Ethyl Vinyl Ether.—Irradiation of toluene in the presence of ethyl vinyl ether either as an equi-volume solution or in the presence of a diluent led to the formation of a complex mixture of 1 : 1 adducts ($M^+ = 164$, m.s.–g.c.), five of which were completely resolved by g.l.c. and which were produced in a time- and solvent-dependent ratio. The most important aspect of the product mixture was to assess the relative proportions of the *ortho*- and *meta*-cycloadducts. The initial ratio of these adducts from equi-volume solutions of the addends was approximately 8.5 : 1 : 2 : 1.5 : 1 (increasing retention time on Apiezon L columns). The relative ratio of the last two components compared to the first three decreased markedly with time of irradiation, and from preparative experiments giving at least 0.5 g of product, together these photo-labile adducts, never constituted more than *ca.* 6% of the total, and hence their isolation was impractical. Both the photo-labile adducts were removed from the chromatogram (*a*) at injection-block temperatures of $\geqslant$280 °C, and (*b*) by addition of *N*-phenylmaleimide to solutions of the adducts: this latter procedure gave trace amounts of a 1 : 1 : 1 adduct ($M^+ = 337$, m.p. 153—156 °C) of *N*-phenylmaleimide, toluene, and ethyl vinyl ether, but did not significantly affect the concentrations of the other three adducts. The n.m.r. spectrum of the 1 : 1 : 1 adduct indicated that the 1 : 1 photo-adduct resulted from *ortho*-attack of the ethyl vinyl ether at both the 1,2- and 2,3-positions of toluene and that the reaction had occurred with *exo*-stereochemistry. The mass spectra of the photo-labile adducts showed facile reversion to starting materials, and from these data we assign the *ortho*-cycloadduct structure (11) to the two products of longest retention time. The effect of solvent polarity on this system was consistent with this assignment,



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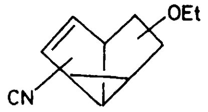
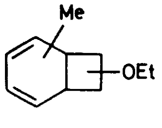


(10)

bearing in mind the deduction from other systems [2,3] that *ortho*-cycloaddition involves a degree of polarity in the transition state. Thus the combined relative yield of these two 1 : 1 adducts at short reaction times in cyclohexane and acetonitrile as diluent was 1 : 1.5.

Of the three photo-stable adducts *ca.* half the major component and the two minor products were thermally converted at 280 °C into an isomeric mixture presumed to be comprised of the bicyclo[3.3.0]octa-2,7-dienes.[13] This thermal lability indicates that there are two isomers in the major product and one of these has the ethoxy-group *endo* in the 7-position. These 1 : 1 adducts were isolated by preparative g.l.c. and, from their n.m.r. spectra and comparison with those reported for other *meta*-adducts of toluene,[5] they are assigned to the regio- and stereo-isomers of the 1-methyl-*meta*-cycloadduct structure (12). From the thermal stability it would seem that all four regio- and stereo-isomers of (12) are formed with the 7-*endo*-product constituting some 40% of the total mixture. This latter assignment is supported by the observation that at temperatures >320 °C this adduct, stable at the lower temperature, also yielded a bicyclo[3.3.0]octa-2,7-diene isomer: this is rationalised by a vinyl cyclopropane–cyclopentene rearrangement at the higher temperature to give the *endo*-6-ethoxy-isomer of (12) which then undergoes the [1,5] sigmatropic shift reaction.[13] The effect of change in solvent polarity on the formation of the *meta*-cycloadducts was minor but in repeat experiments there was a slight (*ca.* 8%) increase in the yield in acetonitrile compared to that in cyclohexane. This result is surprising in view of our own [2,4] and other studies [14] on arene–ethylene systems in which *meta*-cycloaddition is found to be unaffected by change in solvent polarity.



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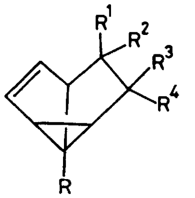


(12) $R = Me$; R^1, R^2, R^3, or $R^4 = OEt$
(13) $R = OMe$; R^1, R^2, R^3, or $R^4 = OEt$
(21) $R = OMe$; $R^1 = R^2 = R^3 = R^4 = Me$

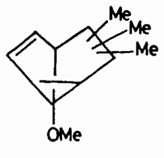
Anisole–Ethyl Vinyl Ether.—Irradiation of an equi-volume mixture of the addends gave two products in a time- and reactant-concentration-independent ratio of *ca.* 1 : 3 (g.l.c. Apiezon L): neither product was affected by the addition of *N*-phenylmaleimide to their solutions. Both products were shown to be 1 : 1 adducts by m.s.–g.l.c. and the components were isolated by preparative g.l.c. The four stereo- and regio-isomers of the 1-methoxy-*meta*-cycloadduct structure (13) are assigned to the 1 : 1 adducts on the basis of their spectroscopic properties (particularly n.m.r. spectra) and comparison with those of analogous adducts of anisole with hydrocarbon ethylenes [6] and of benzene with ethyl vinyl ether.[3] In particular the position of the methoxy-group is deduced in all isomers to be at the 1-position by the absence in the n.m.r. spectra of either a quartet or triplet (*J* 7 Hz) (if the 2-, 5-, or 8-position is substituted) which is the characteristic resonance of the H-1 proton, and arises from coupling to H-2, H-5, and H-8.[5] The presence of both ethylenic protons and all their expected vicinal and allylic couplings also discounts substitution at the 2-, 3-, 4-, or 5-position. The fraction of shorter retention time was judged to be one *meta*-cycloadduct whereas the methyl resonance of the ethyl group of the latter fraction was clearly comprised of three sets of triplets in a ratio of 1 : 1.25 : 2.5 (low to high field). At 280 °C three of the adducts were isomerised but *ca.* 30% of the three-isomer mixture only isomerised at temperatures >320 °C, again consistent with its being the *endo*-7-ethoxy-isomer of (13), and at the higher temperature underwent the vinyl-cyclopropane–cyclopentene rearrangement to yield the *endo*-6-ethoxy-isomer which immediately rearranged by a [1,5] sigmatropic shift to the bicyclo[3.3.0]-octa-2,7-diene derivative.[13]

Routinely with these systems we examined the effect of solvent on the photo-reaction. The ratio of *meta*-cycloadducts is seemingly unaffected by change of this parameter but most surprisingly the yield of products increased markedly in the series cyclohexane ($\Phi = 0.2$) < methanol < ethyl acetate < acetonitrile ($\Phi = 0.4$). The solvent properties which also change in this order in this series are dipole moment [15] and viscosity.[16] This latter solvent feature is considered to be relatively unimportant in the present reaction as the yield of adducts in n-butyl alcohol is, within experimental error, the same as that in methanol: both solvents have similar dipole moments but the former is *ca.* six times as viscous as the latter. In no case did change in solvent result in the formation of products other than those described.

The efficiency of the *meta*-photo-cycloaddition of other ethylenes to anisole has not shown this solvent dependency but in previously reported examples the ethylenes have all been hydrocarbons with ionisation potentials, either determined or predicted to be, appreciably higher than that of ethyl vinyl ether. For direct comparison with the present results, it was, therefore, necessary to study the photo-reactions of anisole with hydrocarbon ethylenes of ionisation potential of *ca.* 8.6 eV; 2-methyl- and 2,3-dimethyl-but-2-ene, with ionisation potentials of 8.8 and 8.5 eV, respectively, are suitable for the present purpose.

The 2-Methyl- and 2,3-Dimethyl-but-2-ene–Anisole Systems.—Irradiation of 2-methylbut-2-ene and anisole produced a time- and reactant-concentration-independent mixture of isomers of the 1-methoxy-*meta*-cycloadduct (14). The basic structure of the 1 : 1 adducts was deduced from the n.m.r. spectrum of the adduct mixture and its comparison with reported data.[4,6] The presence of all the regio- and stereo-isomers was deduced by analysis of the methyl-resonance region and its detailed comparison with the n.m.r. spectra of the two isobutylene–benzene *meta*-cycloadducts and the corresponding four isomers from 2-methylbut-2-ene and benzene: [4,17] the 1-position of the methoxy-group was assigned as outlined above. No evidence was obtained for the presence of an ' ene ' product (15), analogous to that formed between this ethylene and benzene,[4] nor for *ortho*-cycloaddition products. However, it is possible that this latter mode of reaction does occur to a very limited extent, since irradiated solutions of 2-methylbut-2-ene and anisole show weak absorption maxima at 282, 298, 311, and 325 nm, which are considered to be indicative of the presence of the tetraene (16), produced by thermal and/or photolytic-ring opening of the *ortho*-cycloadduct (17). Using published data for extinction coefficients of tetraenes at these wavelengths, however, we estimate that the presence of such compounds is less than 0.5% of the *meta*-cycloadduct mixture.

Three products were produced from the irradiation of equi-volume solutions of anisole and 2,3-dimethylbut-2-ene. Analysis of the mixture by m.s.–g.l.c. showed that the most abundant component (85%) was a 1 : 1 adduct of the reactants whereas the parent ions and fragmentation patterns of the minor products were consistent with the ethylene dehydro-dimers (18), (19), and (20), recently reported by Cantrell, obtained from the irradiation of benzonitrile and this ethylene.[9] The 1 : 1 adduct isolated by preparative g.l.c. was thermally stable and had spectroscopic properties entirely consistent with structure (21). The methoxy-group residing specifically on the 1-position was again deduced by the absence of the characteristic H-1 proton resonance in the n.m.r. spectrum and from the doublet appearance of the H-5 resonance ($J_{4,5}$ 3 Hz) with no 7 Hz coupling from H-1. Decoupling experiments and successive addition of a europium shift-reagent confirmed this assignment. The absorption spectrum of irradiated solutions of the addends had absorptions at 304, 316, and 332 nm which is again attributed to the presence of a tetraene formed by ring-opening of an *ortho*-cycloadduct but the concentration of this compound was considered to be less than 2% of that of (21). Formation of a 1,4-acyclic ' ene ' product was not observed.[4,18]



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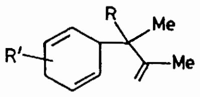
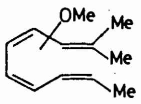


(15) R = H, R' = OMe

(26) R = Me, R' = H



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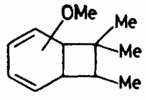

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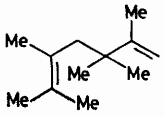

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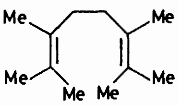

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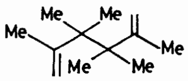
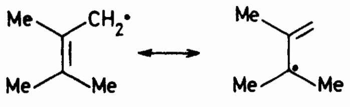


(20)

Photo-cycloaddition modes of ethylenes to benzene and its derivatives

Arene	I.P. (eV)	Ethylene	ΔI.P. (addends) (eV)	Photo-products
Benzonitrile	10.02	ethyl vinyl ether	1.42	regio- and stereo-isomers of *ortho*-cycloadducts
Benzene	9.24	ethyl vinyl ether	0.64	*ca.* 2 : 1 ratio of efficiencies of *ortho*- to *meta*-cycloadditions [3]
Toluene	8.82	ethyl vinyl ether	0.22	*ca.* 1 : 4.5 ratio of efficiencies of *ortho*- to *meta*-cycloadditions
Anisole	8.54	ethyl vinyl ether	0.06	regio- and stereo-isomers of 1-methoxy-*meta*-cycloadduct
Anisole	8.54	2-methylbut-2-ene	0.26	regio- and stereo-isomers of 1-methoxy-*meta*-cycloadduct
Anisole	8.54	2,3-dimethylbut-2-ene	0.04	1-methoxy-*meta*-cycloadduct and dehydro-dimers of the ethylene

The photo-addition of these two hydrocarbon ethylenes was examined in cyclohexane, ethyl acetate, and acetonitrile. In contrast to the reactions with ethyl vinyl ether, but similar to those reported with other hydrocarbon ethylenes, the efficiency of the *meta*-cycloaddition of 2-methyl- and 2,3-dimethyl-but-2-ene to anisole was not significantly affected by change in solvent. The only observed trend was that in the series, the yield of the ethylene dehydro-dimers from 2,3-dimethylbut-2-ene increased markedly to the extent that in acetonitrile these became the major photo-products. The formation of the dehydro-dimers is considered to involve hydrogen abstraction by the photo-excited arene from the ethylene followed by combination of the radical (22).[9] An explanation of the presently observed effects may lie in the reduction in solvent viscosity in the series, but is more likely to reflect the hydrogen-atom donor ability of the solvent. Thus in cyclohexane, combination of the radicals to give the dehydro-dimers has to compete with hydrogen abstraction, whereas in acetonitrile the latter process is far less favourable and hence the yield of (18), (19), and (20) is significantly increased.



(22)

The benzene–ethyl vinyl ether system has been fully described.[3,11] The results are presented along with those from the present study in the Table.

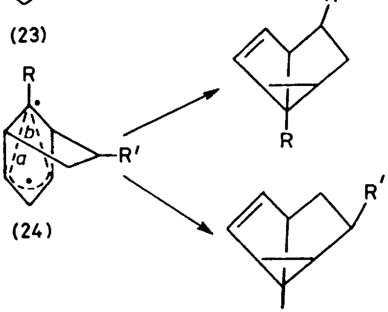
DISCUSSION

The proposed relationship between ionisation potential differences of the addends in ethylene–benzene systems and the relative efficiency of mode of reaction (*i.e. ortho*- or *meta*-cycloaddition) has received much attention in recent literature.[1,12,19,20] In general, within a series of structurally related ethylenes, as ΔI.P. increases so does the relative efficiency of *ortho*-cycloaddition, and for addends of similar ionisation potential, only the *meta*-process is observed. The present study was undertaken to ascertain if a similar relationship would be observed for ethylenes of relatively low ionisation potential with benzene derivatives which had a spread of ionisation potentials: the investigation revealed quite unexpected solvent effects for two *meta*-cycloadditions. The data for the present systems are summarised in the Table. Within the arene–ethyl vinyl ether series, as the ΔI.P. value decreases the relative efficiency of the *ortho*-cycloaddition decreases until with anisole only the *meta*-cycloadducts are observed. However, it should be realised that the value of ΔI.P. can only serve as a broad guide to indicate which mode will be preferred within a particular series of ethylenes and arenes. Thus the cycloaddition of 2-methylbut-2-ene to anisole should, strictly in numerical values of ΔI.P. of the addends, be expected to be very similar to those of toluene and ethyl vinyl ether, but in the former case the only evidence for *ortho*-cycloaddition lies in the observation of absorption bands attributed to the tetraene (16). Even with cyclopentene as addend to anisole, where the ΔI.P. value is 0.48 eV, no *ortho*-cycloadducts are reported.[6,14] Indeed the only ethylenes which have been observed to yield such products from anisole are acrylonitrile [21] and maleimide [22] where the ΔI.P. values are 2.34 and 1.74 eV, respectively. Nonetheless, the present results indicate that the proposals based on benzene and a series of ethylenes [2] may be extended to other arenes. Thus only for systems in which ΔI.P. values are relatively large is *ortho*-cycloaddition observed and addends of similar ionisation potential yield essentially only *meta*-cycloadducts. The converse of the former conclusion does have one exception, and this is the *meta*-cycloaddition of vinylene carbonate to benzene,[20] a system in which ΔI.P. is 0.84 eV: but we have previously discussed why this exception could be more apparent than real.[1]

In all the systems studied here, the *meta*-cycloadditions occur at the 2,6-positions of the substituted benzenes and as far as the *ortho*-cycloaddition to benzonitrile is concerned, this is largely, if not exclusively, a 1,2-process. The former observations are consistent with those of Srinivasan and his co-workers [5,6] with methyl- and methoxy-benzenes and hydrocarbon ethylenes. Since *endo*-stereoisomers of the *meta*-cycloadducts predominate or are exclusive, this specificity of attack has been reasonably used as evidence for the involvement of an *endo*-sandwich exciplex [*e.g.* (23)] in the reaction pathway.

Although it was only with toluene and ethyl vinyl ether that the *meta*-cycloaddition reported here had any degree of regio- or stereo-selectivity (*ca.* 40% of the 7-*endo*-isomer) there is no reason to believe that in the present systems such excited state species as (23) are not involved. Indeed, for example with anisole and ethyl vinyl ether, the alternative closures to form the cyclopropane ring [*i.e.* either formation of bond *a* or *b* in (24) leading to the 6- and 7-isomers respectively], following 2,6-addition within the exciplex (23), could explain the lack of any marked regioselectivity of this *meta*-cycloaddition. We have previously noted that prefulvene intermediates (25), possibly polarised, could be involved in *meta*-cycloadditions and that the extent of participation of these species may vary with the addends.[4,23] The lack of regioselectivity could, as above, be used to argue against involvement of (25), but in systems where regioselectivity is observed to any extent it is not obvious why the species analogous to (24) would preferentially ring-close to yield predominantly one or other of the regioisomers (*i.e.* 6- or 7-isomer) and in such cases primary arene rearrangement to (25) followed by regioselective addition of the ethylene, particularly for examples in which this has a polar substituent, is an attractive alternative mechanism. However if this latter pathway is followed to any extent with any of the above *meta*-cycloadditions it poses the question ' why is the arene substituent specifically located in the 1-position of the *meta*-cycloadduct? ' It would be expected, on the basis of the substituent stabilising the intermediate (25), that either the 5- or 8-substituted-*meta*-adduct isomer would be preferred: the former was observed in the addition of *cis*-cyclo-octene to toluene.[24] On the other hand, the specificity for formation of the 1-isomer is nicely explained by a pathway involving a specifically oriented exciplex.[5,6] The situation concerning which features in the addends will predominate and determine the preferred pathway and the resulting selectivities appears to be finely balanced. Ethyl vinyl ether did quench the arene fluorescence in solution weakly and the efficiency decreased in the order benzene > toluene > anisole but no exciplex emission was observed from these systems even in triangular cells at high reactant concentrations in acetonitrile,[25] and no evidence for charge-transfer absorption of a ground state complex of the addends was obtained.

(23)

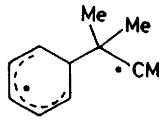


(24)

(25)

A remarkable and unexpected feature of the *meta*-cycloaddition of ethyl vinyl ether to anisole is the enhancement of the process in polar solvents. This feature has not been observed in any other *meta*-cycloaddition.[2-4,14] We have confirmed that this solvent effect appears at present to be restricted to the anisole–ethyl vinyl ether system, and not for anisole and any electron-donor ethylene, since the corresponding reactions with 2-methyl- and 2,3-dimethyl-but-2-ene are unaffected by change in solvent. It should also be emphasised that change of solvent in the anisole–ethyl vinyl ether system did not yield products other than those described and so no evidence was obtained to suggest that the chemistry of an intermediate exciplex is changed in the more polar solvent to yield, for example, ethylene dimers rather than an enhancement or initiation of the *ortho*-cycloadduct formation. Solvent stabilisation of an undetected ground-state complex which has a degree of polarity is unlikely, since the promotional effect is observed in the system where the differences in electron donor–acceptor properties of the addends are least. Similarly it is difficult to appreciate how increase in solvent polarity could affect an excited state complex in this particular system, and in no other, leading to *meta*-cycloaddition, and hence we suggest that it is the stability of the 2,6-bonded intermediate (24),[6] formed by collapse of the exciplex, which may be affected by change in solvent. It may be expected that the polarity of (24) (R = OMe, R′ = OEt) formed from anisole and ethyl vinyl ether would, as a result of the combination of the mesomeric ($+M$) and inductive ($-I$) effects of the methoxy- and ethoxy-groups, respectively, be greater than that of the corresponding species from the benzene–ethyl vinyl ether and anisole–alkene systems, the *meta*-photo-cycloadditions of which have been previously reported not to be affected by change in solvent polarity.[2,3,14] Thus it is proposed that the present unexpected solvent effect on *meta*-cycloadduct yields may be explained in terms of the polarity which may be achieved in the intermediate (24). Such a proposal also accounts for the lack of solvent effect on the photoreactions of anisole with the electron-donor ethylenes 2-methylbut-2-ene and 2,3-dimethylbut-2-ene observed in the present work.

Formation of 1,4-acyclic ' ene ' products (26) from benzene and 1,1-dimethylethylenes is a non-concerted process and is considered to arise *via* an intermediate such as (27) or at least a correspondingly polarised exciplex.[4] Thus the ethylene acts as an electron donor to the excited arene and so, in view of the fact that the charge density in the ring of S_1 (and T_1) anisole is calculated to be even greater than that in the S_0 arene,[26] it would not be surprising if in this case there were little or no electron transfer to the arene and hence the absence of an ' ene ' product from systems involving anisole may be rationalised.



(27)

EXPERIMENTAL

All irradiations were carried out in quartz tubes of varying capacity using radiation from Hanova 15-W low-pressure mercury-arc lamps. The effect of solvent on the irradiation was assessed using solutions 1.1M in arene and 3.5M in the ethylene. Stirring or degassing the irradiated solutions caused negligible effects on the efficiency or linearity of product formation within the time periods used. In all cases it was found essential, in order to obtain reproducible results, to re-distil the ethyl vinyl ether *immediately* before use. The general procedure for preparative experiments was to irradiate an equi-volume solution of the addends and monitor the reaction by g.l.c. After a suitable time period (*ca.* 12—24 h), when product formation was sufficient or when occluded polymeric material on the cell walls had effectively stopped product formation, the starting materials were removed *in vacuo* and recycled if necessary. The residual oil was vacuum-distilled, and where appropriate the components were separated by preparative g.l.c. Unless stated otherwise, ^1H n.m.r. spectra were recorded at 100 MHz.

Benzonitrile–Ethyl Vinyl Ether.—The brown oil (*ca.* 8 gm) from a 15-h irradiation of the addends (200 ml) was vacuum-distilled at 80—95 °C at 0.05 mmHg. The pale yellow distillate was stored at −20° C under nitrogen. The n.m.r. spectrum had resonances at δ 1.23 (3 H, combination of triplets, Me), 2.4—2.7, (2 H, m, methylene on cyclobutane), 2.7—3.3 (1 H, m, allylic methine), 3.4—3.9 (2 H, overlapping q, O=CH_2Me), 4.2—4.7 (1 H, m, CH–O), and 5.7—6.2 (4 H, m, =CH); $\lambda_{max.}$ (cyclohexane) at 276 nm. I.r. absorptions characteristic of the functionality in (6) were observed at 3 040w, 3 010w, 2 970s, 2 930m, 2 870s, 2 210s, 1 640—1 600w, and 1 100s cm^{-1}. The 1 : 1 adduct (6) (1.0 g) in diethyl ether (20 ml) was treated with *N*-phenylmaleimide (1 g). After 24 h colourless crystals of the 1 : 1 : 1 adduct (9) began to separate and after 6 d 1.7 g of product were filtered off. This sample was recrystallised from acetone–ether (40 : 60), m.p. 127—128 °C. The mixture of regio- and stereo-isomers of (9) had n.m.r. resonances at δ 1.25 (3 H, complex t, Me), 1.75—2.10 (1 H, m), 2.15—2.5 (1 H, m), 2.65—2.95 (1 H, m), 2.95—3.15 (1 H, m), 3.25—2.75 (6 H, m), 6.25—6.6 (2 H, quintet of doublets, =CH), 7.10—7.30 (2 H, m), and 7.30—7.55 (3 H, m). Characteristic $\nu_{max.}$ were at 2 230 (CN), 1 780, and 1 715 (C=O of imide in acyclic five-membered ring), and 1 600 cm^{-1} (aromatic C=C).

Toluene and Ethyl Vinyl Ether.—The oil (2.0 g) from irradiation of an equi-volume mixture was dissolved in ether (20 ml) and *N*-phenylmaleimide (0.15 g) added. The solution was allowed to stand at room temperature until the two long-retention-time adducts were no longer evident in the chromatogram (3 d): the mixture was slightly turbid. Removal of the ether to low bulk (*ca.* 5 ml) and addition of 40—60 °C b.p. light petroleum (10 ml) produced a very small quantity of solid material which had $M^+ =$ 337 and m.p. 153—156 °C; the n.m.r. spectrum had the following features: a series of complex multiplets from δ 1.5—3.2 p.p.m. superimposed on which were resonances at 1.15 (3 H, at least 3 superimposed triplets), 1.39 (*ca.* 1.5 H, s), 2.93 (*ca.* 1.5 H, d), 3.22—3.5 (2 H, superimposed quartets), 3.85—4.15 (1 H, m), 5.75—5.95 (1 H, dd), 6.32—6.53 (1 H, dd), 7.16—7.3 (2 H, m), and 7.3—7.55 (3 H, m). The oil obtained following removal of the *ortho*-cycloadducts was distilled (80—90 °C at 2.5 mmHg) and the major component separated by preparative g.l.c. The n.m.r. spectrum (C_6D_6) of this component was consistent with the presence of two *meta*-cycloadducts in *ca.* equal amounts and had resonances centered at 1.1 (3 H, two overlapping triplets approximately 1:1 integral, Me), 1.3 and 1.45 (3 H, combined, s, Me on 1-position), and 3.2 (2 H, two overlapping quartets, OCH_2); these clearly defined resonances were superimposed on multiplets with resonance positions from δ 0.9—4.6 and which integrated for 6 H, further resonances centred at 5.3 (0.5 H, dd, $J_{4,5}$ 2, $J_{4,3}$ 5.5 Hz, H-4 of one isomer), 5.5 (1 H, br d, H-4 of one isomer and H-3 of the other), and 5.8 (0.5 H, dd, $J_{3,2}$ 2, $J_{3,4}$ 5.5 Hz, H-3 of one isomer); $\lambda_{max.}$ (cyclohexane) for the mixture was at 215 nm; $\nu_{max.}$ (liquid smear) 3 060w, 3 030w, 2 980m, 2 920m, 2 860m, 1 595w, 1 450m, 1 345m, and 1 090s cm^{-1}. The minor two light-stable adducts were collected in one fraction by preparative g.l.c. and had spectra which differed only in minor detail from those reported above.

Anisole and Ethyl Vinyl Ether.—The 1 : 1 adduct mixture from anisole and ethyl vinyl ether was distilled (70—80 °C at 0.1 mmHg) and separated into the two components by preparative g.l.c. The n.m.r. spectrum (C_6D_6) of the first fraction, which is one isomer, had δ 1.1 (3 H, t, J 7 Hz, Me), 1.6—2.4 (3 H, m and AB quartet, J_{gem} 13 Hz, H-8 and H-6 or H-7 protons), 2.8—3.5 (4 H, m and q, OCH_2, H-5 and H-2), 3.2 (3 H, s, OMe), 4.2 (1 H, br m, *H*COEt), 5.6 (1 H, m, $J_{4,3}$ 5.5 Hz, H-4), and 5.8 (1 H, dd, $J_{3,4}$ 5.5, $J_{2,3}$ 1.5 Hz, H-3).

The n.m.r. spectrum (C_6D_6) of the second fraction had resonances at δ 1.1 (3 H, three overlapping triplets, Me), 1.4—2.4 (4 H, multiplets), 3.0—3.6 (6 H, m), 3.7—4.4 (1 H, br m), 5.3—5.5 (1 H, m), and 5.6—5.8 (1 H, m). Neither fraction had absorption maxima above 220 nm and each had absorption in the i.r. spectrum characteristic of *meta*-cycloadducts.[4]

Anisole and 2-*Methylbut*-2-*ene*.—The oil from irradiation of this system was distilled at 90—100 °C and 0.01 mmHg. The n.m.r. spectra (C_6D_6) of the mixture had resonances at δ 0.6—1.3 (9 H, nine-line resonance, 3 Me), 1.3—2.5 (3 H, m), 3.1, 3.0, 2.8 and 2.7 (total 1 H), 3.17 and 3.20 (total 3 H, two singlets, OMe), and 5.4—5.8 (2 H, m); $\nu_{\text{max.}}$ 3 060w, 3 030w, 2 940s, br, 1 595w, 1 450m, 1 400m, 1 380m, 1 135m, and 770m cm^{-1}.

Anisole and 2,3-*Dimethylbut*-2-*ene*.—The oil from irradiation of this system was distilled at 110—120 °C and 0.01 mmHg and the 1 : 1 adduct (21) separated from the ethylene dehydro-dimers by preparative g.l.c.; δ (60 MHz, C_6D_6) 0.75 (3 H, s, Me), 0.90 (3 H, s, Me), 0.95 (3 H, s, Me), 1.1 (3 H, s, Me), 1.8—2.0 (2 H, m), 2.6 (1 H, d, $J_{4,5}$ 3 Hz), 3.1 (3 H, s, OMe), and 5.5—5.8 (2 H, m), $\nu_{\text{max.}}$ 3 060w, 3 030w, 2 940s,br, 1 595w, 1 450m, 1 400m, 1 390m, 1 375m, 1 365m, 1 140m, 1 125m, 1 055m, and 745m cm^{-1}.

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