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REGIO- AND STEREO-SELECTIVITIES OF THE *ORTHO* AND *META* PHOTOCYCLOADDITION REACTIONS OF ETHYLENES TO BENZENE AND ITS SIMPLE DERIVATIVES

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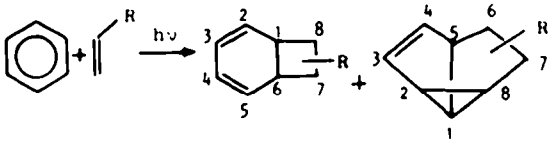
Abstract—The photoreactions of benzene, toluene, anisole, and benzonitrile with acrylonitrile, methacrylonitrile, and vinyl acetate, and of toluene and *o*- and *p*-xylene with maleic anhydride are described. The acrylonitriles do not react with benzonitrile but yield mixtures of *ortho* photocycloadducts with the other arenes. Contrary to previous findings both *exo* and *endo* stereoisomers of the *ortho* cycloadducts of benzene and acrylonitrile are formed: the reaction is selective towards the *exo* isomer but the stereoisomers from methacrylonitrile and benzene are formed with approximately equal efficiencies. Complex mixtures of regio- and stereoisomers of the *ortho* cycloadducts are formed between toluene and the acrylonitriles but their addition to anisole is more selective and in acetonitrile essentially only 1,2-attack of the ethylene on the arene is observed. The 2:1 photoadducts of maleic anhydride with toluene and *o*- and *p*-xylene reflect formation of two regio *ortho* photocycloadducts in each case. The variation in the ratios of these isomers with temperature and light intensity is interpreted in terms of the differing photolabilities of the 1:1 adducts and their reactivities towards the thermal addition of the second molecule of maleic anhydride. Vinyl acetate undergoes 1,2-cycloaddition to benzonitrile but with the other arenes, *meta* cycloadducts are favoured. These latter additions are specifically 2,6- with respect to toluene and anisole but there is little regioselectivity with respect to the ethylene although the 7-*endo* acetate of the *meta* cycloadduct with benzene does constitute 60% of the reaction mixture.

Since the first reports which described the *ortho* and *meta* photocycloadditions of ethylenes to benzene and its simple derivatives to give bicyclo[4.2.0] octa-2,4-dienes (1) and tricyclo[3.3.0.$0^{2,8}$]oct-3-enes (2) respectively,[1-4] there have appeared many accounts which have discussed a variety of features of these intriguing processes[5] and attempts have been made to elucidate the factors which influence the reaction efficiencies and selectivities.[6-11] For many systems the two reaction modes compete but the *ortho* cycloaddition reaction is greatly favoured in cases where the addends form an obvious electron donor–acceptor pair.[5] Thus it has been suggested that for benzene, the quantum yield of the *ortho* cycloaddition is greater than that of the *meta* process for ethylenes which have ionisation potentials greater than 9.6 eV and less than 8.65 eV.[12] Although there is a notable exception to this "rule",[13] from ionisation potential differences of the addends, it has been possible to predict successfully for many systems the preferred mode of ethylene–benzene photocycloaddition.[9,10] Published data concerning regio- and stereoselectivities of these reactions are, however, sparse particularly for the *ortho* cycloaddition, and yet such fundamental information is essential in meaningful mechanistic discussion, and if the processes are to be exploited as synthetic routes to systems of types 1 and 2.



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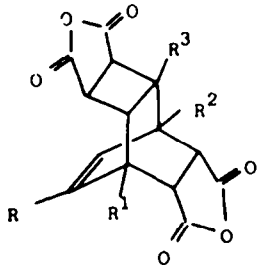
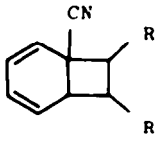
We have recently determined the stereochemistry of several *ortho* cycloadducts of both electron donor and electron acceptor ethylenes with benzene and although for some systems the reaction is apparently stereospecifically *exo*, in other examples both stereoisomers are formed with little selectivity.[14] The regio- and stereoselectivities of *ortho* cycloaddition of ethylenes to benzene derivatives has received very limited attention. It would appear from the structures of the 2:1 adducts (3) from irradiation of solutions of maleic anhydride in alkylbenzenes that the intermediate *ortho* photocycloadduct results from 2,3- and/or 3,4-ethylene attack: the proportions are reported to be temperature dependent.[15] In contrast *ortho* cycloaddition of ethylenes to the benzonitrile nucleus occurs specifically at the 1,2-positions to give derivatives of 4[16,17] although reaction at the nitrile function to form azetines (5) and azabutadienes (6) is the dominant process with ethylenes having pronounced electron donor properties:[17-19] these results are interpreted in terms of preferred orientations within intermediate exciplexes.[17] Similar specific 1,2-attack of acrylonitriles to anisoles has been reported but no structural proof was presented and seemingly other orientations of reaction were not considered.[20,21]



(3) R^1s = H or alkyl

(30) R^1=R^2=Me, R=R^3=H

(31) R=R^3=Me, R^1=R^2=H



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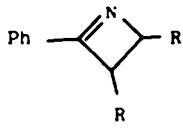

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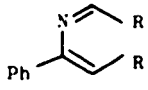

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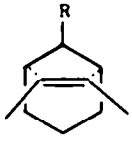
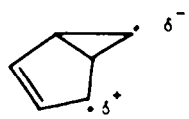


(7) R=Me or OMe



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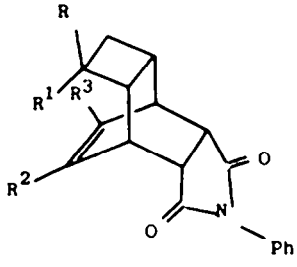
The regioselectivity of the *meta* cycloaddition of symmetrically substituted ethylenes to benzene derivatives has received some detailed investigation. The *meta* cycloadducts of several ethylenes with methoxy and methyl benzenes reflect specific attack at the arene 2,6-positions and *endo* stereochemistry is preferred.[6,7] The observations are rationalised in terms of the involvement in the reaction pathway of an *endo* sandwich exciplex (7). There are, however, notable exceptions to this specificity of reaction and in other cases, the orientation of substituents in the *meta* cycloadduct is best explained in terms of substituent stabilisation of an intermediate polarised diradical (8) which is formed by photorearrangement of the arene and which subsequently undergoes concerted ethylene addition to yield the *meta* cycloadducts (2).[9,22] The regioselectivity of the *meta* cycloaddition with respect to an unsymmetrically substituted ethylene (i.e. whether the 6- or 7-substituted isomer of 2 is formed preferentially) has only been determined for a relatively few systems and the results are somewhat conflicting. For example whereas the addition of propene is deduced to be specific giving the *exo* and *endo* 7-methyl derivatives of 2,[23] isobutene[9] and methylene cyclobutane[24] give approximately 1:1 mixtures of the 6- and 7-substituted isomers. Determination of ethylene regioselectivity is important as this could assist in assessing the contribution of the differing mechanistic pathways.

Thus although the preferred modes (i.e. *ortho* or *meta*) of photocycloaddition of ethylenes to benzene and its simple derivatives are largely predictable, only for a relatively few systems have the selectivities of the processes been determined but even in such cases the results, particularly for the *ortho* cycloadditions, may not be too meaningful as the differential photolabilities of the isomers, which we now know can be most marked,[25] have not been given sufficient consideration. We now report on the photoaddition reactions of a variety of arene-ethylene systems and thereby present a better perspective than previously available of the regio- and stereo-selectivities of the *ortho* and *meta* photocycloaddition reactions. In particular we have sought to determine if, as published data suggests and appears to be the case for the *meta* process, there is an underlying pattern of orientation and stereochemistry of the *ortho* cycloaddition of ethylenes to benzenes.

RESULTS AND DISCUSSION

The systems studied in detail involved benzene, toluene, anisole, and benzonitrile with acrylonitrile, methacrylonitrile and vinyl acetate, and maleic anhydride with toluene and *o*- and *p*-xylene. The results are compared with those we recently reported for the photoaddition of ethenyl ethers to the above arenes.[10,11]

All irradiations were carried out in quartz apparatus using low pressure mercury-arc lamps. The effect of air or nitrogen on product formation was negligible under our reaction conditions. Undiluted equimolar solutions of the addends were used in preparative experiments but in some systems amounts and ratios of adducts were markedly dependent upon the diluent and period of irradiation. Thus, in general, *ortho* cycloaddition was favoured in polar solvents and all *ortho* cycloadducts were to some extent both thermally and photochemically labile. The irradiated solutions were analysed by open tubular glc (Carbowax 20M, OV101, and Squalane SCOT columns) but where thermal degradation of the *ortho* cycloadducts was suspected, these results were supported by hplc analysis (Partisil PX10/20). By such means it was observed that most of the substituted benzenes gave mixtures of varying complexity of 1:1 adducts (MS/glc). Because of the lack of isomer resolution by preparative chromatographic methods and since in some cases isomerisation and/or decomposition of the photo-products by these techniques was suspected, it proved impractical to obtain pure samples of individual isomers from all systems but the *ortho* cycloadducts were conveniently isolated by their quantitative reaction with N-phenylmaleimide to give 1:1:1 adducts (9) which could be separated by flash chromatography and/or fractional crystallisation. The spectroscopic features of *ortho* and *meta* cycloadducts of benzenoid compounds and ethylenes and the former adducts' dienophile derivatives which allow their ready identification, have been described in detail in several reports[26] and hence only the more noteworthy aspects will be presented here.



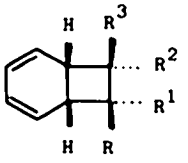
(9) R and/or R^1=ethylene substituent groups
(14) R=R^2=R^3=H, R^1=CN
(15) R=CN, R^1=R^2=R^3=H
(16) R or R^1=H or CN, R^2 or R^3 = Me
(26) R=CN, R^1=Me, R^2=R^3=H
(27) R=Me, R^1=CN, R^2=R^3=H

Consistent with the previous proposals concerning the directing effect of electron donor–acceptor properties of the addends on the reaction mode,[12] both acrylonitrile and methacrylonitrile gave only *ortho* cycloadducts with benzene, toluene and anisole whereas with vinyl acetate as the ethylene, the *meta* mode of cycloaddition predominated or was exclusive with these arenes but again only *ortho* cycloadducts were formed with benzonitrile. Surprisingly benzonitrile did not undergo photoaddition to the acrylonitriles.

Ortho Cycloaddition

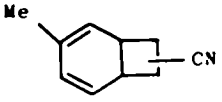
Acrylonitrile-arene systems. The *ortho* cycloaddition of acrylonitrile to benzene was first described by Job and Littlehailes in 1968,[2] and the adduct has been deduced to have exclusively *exo* stereochemistry.[14] In view of the marked photolability differences recently observed for the stereoisomers of an ethylene-benzene *ortho* cycloadduct,[25] this system has been re-examined at very short reaction times and under analytical conditions likely to resolve the stereoisomers. By such means, two 1:1 adducts (M^+ = 131 mu ms/glc) of benzene and acrylonitrile were detected in an initial ratio of 5:1. The minor isomer was photolabile under its conditions of formation and rapidly reached a low photostationary concentration such that from preparative experiments, it constituted < 5% of the mixture: this and its poor resolution by packed column glc accounts for its lack of detection previously.[2,14] The ratios of product formation were supported by hplc analysis and the isomers were isolated essentially pure by flash chromatography. Spectroscopic data of the adducts were consistent with both arising from *ortho* cycloaddition and hence they are the *exo* and *endo* stereoisomers **10** and **11** respectively. Since the more photostable major adduct has been deduced by unambiguous chemical methods to be the *exo* stereoisomer (**10**),[14] it would appear that the minor product is the *endo* isomer (**11**). It is interesting to note here that the electron donor ethylene, 2,3-dihydrofuran, like acrylonitrile, yields both stereoisomers of the *ortho* photocycloadduct with benzene but in contrast to the present system, with the ethenyl ether it is the *endo* isomer (**12**) which is formed with the greater photochemical efficiency and is relatively photostable whereas the *exo* product (**13**) rapidly reaches a photostationary state. At present there is no obvious feature to account for these differing photolabilities. The benzene–acrylonitrile mixture was quantitatively converted into a 5:1 mixture (hplc) of 1:1:1 adducts with N-phenylmaleimide and these isomers were isolated with > 98% purity again by flash chromatography. Spectroscopic and accurate mass data of each product were in agreement with the general 1:1:1 adduct structure (**9**). Consistent with an *endo* orientation of the nitrile group in **14**, the resonance of one of the ethenyl protons in the ^{1}H NMR spectrum was perturbed in the minor isomer, and the signal between δ 6.38 and 6.60 ppm appears as a multiplet and not as an overlapping doublet of doublets.[14,27] Surprisingly, however, the ^{1}H NMR spectrum of the N-phenylmaleimide adduct of the major photoproduct shows two ^{1}H "triplet" signals between δ 6.40–6.52 and 6.68–6.78 ppm. It is not obvious how the *exo* nitrile group in the 1:1:1 adduct (**15**) could perturb one of the ethenyl protons sufficiently to give a difference in chemical shift of the two protons of 0.27 ppm. This aspect of the 1:1:1 adducts continues to be investigated but confirmation that the two protons are present in the same molecule was demonstrated by their spin–spin coupling. Although the formation of both stereoisomers was promoted in polar solvents, their relative rates of production remained essentially constant.

Irradiation of equimolar amounts of toluene and acrylonitrile gave a complex mixture of nine 1:1 adducts (M^+ = 145 m.u. MS/glc) of which three constituted approximately 60% of the total product. Hplc resolved the mixture into three fractions of ratio 4:1:2 (elution sequence on Partisil PX10/20) and these were isolated free from each other by flash chromatography. The two major fractions reacted quantitatively and readily with N-phenylmaleimide while the minor product required prolonged refluxing in ethanol with the dienophile to give a crystalline product. The ^{1}H NMR spectrum of the Diels–Alder product of the adduct fraction of intermediate abundance showed the presence of two resonances (total integral 3H) at δ 2.1 and 2.15 ppm (approximate ratio 2:1) which are assigned to two Me groups residing on the ethylenic bond in the 1:1:1 adduct (**16**). Confirmation of the assignment was provided by the one ethenyl proton resonance at 5.95–6.2 ppm which appeared as a doublet of multiplets. Thus this fraction is comprised of two 1:1 toluene-acrylonitrile adducts in which the ethylene has attacked at the 3,4-positions of the arene giving **17**. It was not possible from the available data to determine if the two isomers arose from differing regio- or stereo-chemistries with respect to the nitrile group. The major Diels–Alder product (m.p. 216–217°) was shown by hplc to be a single component. The ^{1}H NMR spectrum of this adduct had only one Me proton signal and from its resonance position (1.52 ppm) and that the ethenyl protons appeared as a two proton triplet (δ6.40–6.56 ppm) it was deduced that neither of the ethenyl nor allylic positions were substituted, and thus this *ortho* isomer results from 1,2-attack of acrylonitrile on to toluene. Further, the apparent lack of perturbation of the ethenyl protons in the N-phenylmaleimide adduct suggests that the addition has occurred with *exo* stereochemistry and hence structure **18** is assigned to the major adduct of acrylonitrile and toluene. The 1:1:1 adduct of the minor photoproduct again had but a single Me proton resonance (δ1.58) in the ^{1}H NMR spectrum and is hence considered to be only one regioisomer of the *ortho* cycloadduct. Two ethenyl



(10) R=CN, R^1=R^2=R^3=H
(11) R^1=CN, R=R^2=R^3=H
(12) R=R^3=H, R^1-R^2=-O-CH_2-CH_2-
(13) R^1=R^2=H, R-R^3=-O-CH_2-CH_2-

protons were evident (δ6.18–6.55 and 6.62–6.93 ppm) and had both vicinal and allylic splittings so again the Me group must reside on the 1- or 6-position. The perturbation of one of the ethenyl protons suggests *endo* stereochemistry of the nitrile group and hence structure **19** is assigned to this minor *ortho* cycloadduct. Thus in the photoreaction of acrylonitrile to toluene, although there is a preference for 1,2-addition, products from the 3,4-orientation of attack constitute some 30% of the overall process and *exo* stereochemistry appears to be favoured. The reaction efficiency and selectivity were essentially unaffected by change in solvent polarity.



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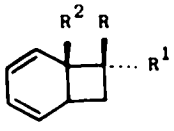
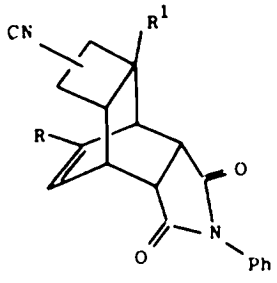


(18) R=CN, R^1=H, R^2=Me
(19) R=H, R^1=CN, R^2=Me
(20) R or R^1=H or CN, R^2=OMe
(24) R=CN, R^1=Me, R^2=H
(25) R=Me, R^1=CN, R^2=H
(28) R or R^1=CN or Me, R^2=OMe
(29) R or R^1 = -OCOMe, R^2=CN

The photoaddition of anisole and acrylonitrile in acetonitrile has been described by Ohashi *et al.* to yield "a mixture of stereoisomers of the [2 + 2]cycloadduct" (**20**):[20] thus specific 1,2-, 1',2'-attack of the ethylene on to the arene is reported. Although polar solvents are known to promote the *ortho* photocycloaddition process, they have not previously been reported to influence the regio- or stereo-selectivity of the process. Irradiation of equimolar mixtures of the addends or a solution of the ethylene (1.0M) and arene (0.1M) in cyclohexane gave four 1:1 adducts (M^+ = 161 m.u. MS/glc) of which two constituted 95% of the mixture: hence the reaction with anisole is considerably more selective than that with toluene. The ratio of the two major products was 3:1 from the undiluted mixture and 3:2 in cyclohexane solution. Irradiation of this system in acetonitrile produced a remarkable change in the reaction selectivity as the major 1:1 adduct effectively became the sole product but was formed with approximately the same efficiency as in the hydrocarbon solvent. The ^{1}H NMR spectrum of the mixture showed that the major isomer had resulted from 1,2-addition of the ethylene on to the arene (i.e. the –OMe group was on the 1- or 6-positions of the bicyclo[4.2.0]octa-2,4-diene system) whereas the adduct which comprised 25% of the mixture had the OMe group on an ethylenic bond. The minor adducts were present in approximately equal amounts and the OMe proton resonance positions indicated again a 1,2- and a 2,3- or 3,4-attack on the arene. Resolution of the 1:1 adduct components by preparative chromatography was unsatisfactory but the mixture reacted quantitatively with N-phenylmaleimide to give a mixture of 1:1:1 adducts (ratio 3:1), which were isolated by flash chromatography. Spectroscopic properties of the major 1:1:1 adduct (**21**) confirmed that the 1:1 photoadduct had the OMe group at the 1- or 6-positions (δ for –OMe at 3.32 ppm). The 2H ethenyl proton multiplet (δ6.40–6.65 ppm), in **21** however, indicated the presence of stereo and/or regio isomers involving the nitrile function. The Diels–Alder product of the second major photo-product was deduced to have structure **22** since only one ethenyl proton resonance was evident (4.9–5.1 ppm double doublet) and the singlet at 3.63 ppm for the OMe protons confirmed the presence of this group on the ethylenic bond. Hence



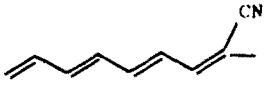
(21) R=H, R^1=OMe
(22) R=OMe, R^1=H

in this photoadduct the reaction has involved the 3,4-positions of the arene. Thus the regioselectivity of the photoaddition of anisole to acrylonitrile is remarkably dependent upon the nature of the solvent and in particular the reaction is essentially specific in acetonitrile and involves the arene 1,2-positions. In cyclohexane this specificity is lost and addition at the 3,4-position becomes significant although, as noted above, the efficiency of formation of the 1,2-adduct is of the same order in each diluent. One interpretation of these observations is that the most polar electron donor–acceptor intermediate complex of the addends involves the 1,2-positions of the arene and this orientation is favoured in the more polar solvent. Yet the efficiencies of formation of the 1,2-product in the two solvents are not dramatically different which more suggests an inhibition of the 3,4-addition in the polar solvent rather than an enhancement of the former mode of reaction in acetonitrile. Although the solvent effects may not be fully understood, such a pronounced promotional effect on the selectivity does make the reaction more attractive as a synthetic step to substituted bicyclo[4.2.0]octa-2,4-dienes.

In view of the difficulty experienced in assigning the stereochemistry of the acrylonitrile adducts, the photoaddition reactions of methacrylonitrile were investigated with these arenes as the methyl group would provide a further "tag" by which to determine structures.

Methacrylonitrile-arene systems

Irradiation of mixtures of methacrylonitrile and benzene in the absence and presence of a diluent gave two 1:1 adducts (M^+ = 145 m.u. MS/glc) in an essentially time invariant ratio of 5:4. Mixtures subjected to prolonged irradiation were yellow and had absorptions at 301, 316 and 332 nm: this is interpreted as the formation of tetraenes (**23**) by the ring opening of the *ortho* ethylene–arene cycloadducts.[9] Use of polar solvents (MeOH



(23)

and MeCN) increased the rate of adduct formation by some twofold compared to reactions in diethyl ether or cyclohexane. Both isomers had characteristics of *ortho* cycloadducts: thus they decomposed readily to starting materials both thermally and under electron impact, and reacted quantitatively with dienophiles. The adduct mixture was isolated free from polymeric materials by vacuum distillation and the ^{1}H NMR spectrum of such samples confirmed the presence of the two stereoisomers **24** and **25**. By analogy with the spectra of the adducts of benzene and methyl methacrylate, the two singlet resonances at 1.56 and 1.61 ppm (integral 5:4 respectively) in the present mixture are assigned to the *endo* and *exo* Me groups respectively: this was confirmed by successive addition of a europium shift reagent when it was observed that the more intense Me resonance was that more greatly affected which reflects an easier access of the europium to the nitrile function in the major isomer. It proved impractical to resolve the adduct mixture completely but their N-phenylmaleimide adducts were successfully isolated in >98% purity (hplc) by fractional crystallisation from ethanol. From the spectroscopic data of the major and minor 1:1:1 adducts their structures were deduced to be **26** and **27** respectively and hence the above stereochemical assignments for the photoadducts were confirmed. Thus the introduction of a Me group on to acrylonitrile has essentially removed the stereoselectivity of the addition of this ethylene to benzene but has produced stereoisomers of comparable photostabilities: this was observed for both direct and benzene sensitised irradiations. That photo ring opening of the *ortho* cycloadducts **24** and **25** does occur is evidenced by the tetraene absorptions of the irradiated solutions but significantly each isomer has similar reactivity in this respect and this is much lower than that of the *endo* isomer (**11**) of benzene and acrylonitrile. Yet not in all cases does such methyl substitution on the ethylene have this profound effect for it is noteworthy here that the *ortho* photocycloadducts of methyl acrylate and methyl methacrylate with benzene have very similar characteristics and each gives a 2:1 stereoisomeric mixture with the carbomethoxy groups in the *exo* and *endo* orientations respectively.[14] Although there is no obvious rationale for these data, they do serve to emphasise that small structural changes in the addends can have pronounced effects on addition selectivities of arene–ethylene systems and on the photostabilities of the *ortho* cycloadduct stereoisomers.

The mixture of photoproducts from methacrylonitrile and toluene was complex and resolved into seven 1:1 adduct components (M^+ = 159 m.u. MS/glc) by open tubular glc. The composition of the mixture was little affected by change in solvent polarity of the reaction media and typical of *ortho* cycloadducts, all components underwent facile retroaddition on electron impact and reacted, albeit with very different rates, with dienophiles. Preparative chromatography gave only partial resolution of the mixture but the ^{1}H NMR spectrum of the distilled mixture was consistent with approximately 25% of the adducts having the aryl Me group at the 1- or 6-positions in **1** and the remainder having this Me on the 1,3-diene system. Thus the *ortho* cycloaddition in this system appears essentially random with no directing effect being apparent.

The photoaddition of anisole to methacrylonitrile in acetonitrile has been reported to give stereoisomers of **28**[21], and hence is regiospecific with respect to both the ethylene and arene. Again we have observed that the selectivity of the reaction is markedly solvent dependent but in this case the effect was not so dramatic as with acrylonitrile as addend. From neat mixtures of anisole and methacrylonitrile or in cyclohexane or acetonitrile solutions four 1:1 adducts (M^+ = 175 m.u. MS/glc) were formed with ratios of 6:3:1:3, 4:2:1:2, and 16:2:1:2 (elution on OV101) respectively. All four products had properties characteristic of *ortho* cycloadducts and the rates of formation of the major products were solvent independent. Four OMe proton resonances in a ratio of 6:3:1:3 (neat mixture) at δ 3.07, 3.13, 3.52 and 3.58 respectively were evident in the ^{1}H NMR spectrum of the mixture: the former two are assigned to OMe groups on the 1- or 6-positions whereas the latter two are considered to result from the group on the 1,3-diene system. Hence the products reflect a considerable degree of 1,2-regioselectivity in the addition particularly if the reaction is carried out in acetonitrile. The three minor components reacted readily with N-phenylmaleimide and the ^{1}H NMR spectra of the 1:1:1 adducts showed that in two of the isomers (ratio 3:1), the OMe group resided on the ethylenic bond and hence reflected that their precursor photoadducts had been formed by 3,4-attack of the ethylene on to anisole. As expected the third minor 1:1:1 adduct had the OMe group on saturated carbon. The ^{1}H resonance of the Me group geminal to the nitrile in these Diels–Alder adducts occurred as a singlet at 1.6 ppm. Comparison of these data with those from the benzene-methacylonitrile adducts suggests that the stereochemistry of the minor adducts is *endo* with respect to the nitrile function. The major 1:1 photoadduct from this system reacted more slowly than the minor isomers with N-phenylmaleimide. The ^{1}H NMR spectrum of this product showed, as expected, that the OMe group resided neither on the ethylenic nor allylic positions and hence confirmed that the major photoadduct had structure **28** but the Me–C–CN proton resonances indicated a mixture of *exo* and *endo* stereoisomers in an approximate ratio of 2:3 respectively with respect to the nitrile function. Thus the photoaddition of methacrylonitrile to anisole is regioselective with the major reaction occurring by 1,2-attack and the 3,4-process making up the remainder. The selectivity is very dependent on solvent and the former mode of reaction is favoured to

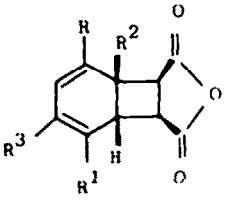
almost 80% in acetonitrile. It is significant that for both acrylonitriles the regioselectivity of the photoaddition is greater for anisole than toluene and only with the former arene is this increased further by a polar solvent. The observations may indicate that as the difference in electron donor–acceptor properties of the arene and ethylene increases, the greater resultant interaction of the addends causes the degree of orientational selectivity in any intermediate ground or excited state complex to increase. Thus it is to be expected that the larger the difference in donor–accept properties of the addends, the more likely the favoured orientation will be "held" and this will be reflected in the degree of regioselectivity of the *ortho* cycloaddition: the favoured orientation would appear to be 1,2- with respect to the arene. This proposal is supported by our recent studies with electron donor ethylenes in which it was observed that the *ortho* cycloaddition of ethyl vinyl ether to benzonitrile was regiospecifically 1,2- but with toluene as the arene, 1:1 adducts from both 2,3- and 1,2-attack were observed. To investigate this further the photoreactions of vinyl acetate with benzonitrile were re-examined.

Vinyl acetate–benzonitrile

Consistent with predictions based on ionisation potential differences of the addends this system has been reported to yield the 1,2-, 1'2'-cycloadduct **29** (no stereochemical assignment) as the major product (61%) with regio and stereoisomers of this same gross structure making up "a large proportion of the remainder of the mixture":[17] our results essentially substantiate these findings. Thus irradiation of mixtures of the addends gave five 1:1 adducts (M^+ 189 m.u.) in a ratio of 60:30:5:2:3. All adducts reacted with dienophiles and fragmented to starting materials in the mass spectrometer and hence were deduced to arise from *ortho* cycloaddition. The ^1H NMR spectrum of the mixture indicated two major isomers (ratio 2:1 of $-O-CO-CH_3$ proton resonances at 2.15 and 2.0 ppm respectively) and the overall integration shows that both major products had resulted from 1,2-addition on to the arene. The adduct mixture was labile in air at room temperature but reacted quantitatively with N-phenylmaleimide to give a mixture of 1:1:1 adducts. Isolation of the major 1:1:1 adducts (M^+ 362 m.u.) was achieved by fractional crystallisation from ethanol and from their ^1H NMR spectra and their comparison with those of the N-phenylmaleimide products of the *ortho* cycloadducts of benzonitrile and ethyl vinyl ether and of benzene and vinyl acetate, it was concluded that the major 1:1 benzonitrile–vinyl acetate adduct was formed by 1,2-, 1'2'-attack with *exo* sterochemistry and that the adduct formed in 30% abundance was its *endo* stereoisomer. The amounts of the minor products prevented their isolation but since no ^1H resonance was observed in the mixture at *ca.* δ 7.3, it is concluded that phenyl azetines and their derived products are absent,[17] and hence no reaction at the nitrile function had occurred.

Maleic anhydride–methylbenzenes

The differing photolabilities of the isomers of *ortho* cycloadducts and their variable rates of reaction with dienophiles which have been observed from some of the present systems, are directly relevant to the interpretation of the results of photoadditions of maleic anhydride to alkylbenzenes.[15,28] In these systems the 1:1 *ortho* photocycloadduct is never isolated but the orientation of the addition is deduced from the structure of the 2:1 adduct and with methyl benzenes has been shown to vary with the temperature of the reaction.[15] This feature could be a reflection of the differing reactivities of the *ortho* cycloadduct regioisomers with the second molecule of dienophile or a result of temperature effects on addend orientations in intermediate complexes. In order to assess if differing photo and thermal labilities are also important features of these systems, the benzophenone sensitised photoaddition of maleic anhydride to toluene and *o*- and *p*-xylene has been examined using two light intensities and at 20° and 100°. The 2:1 adduct structures (3) were established by analytical and spectroscopic data. The regioisomers were separated by fractional crystallisation from acetone but their ratios were estimated by ^1H NMR spectroscopy on the crude photoproduct. The results of irradiation ($\lambda > 290$ nm) of these systems previously outlined were essentially reproduced.[15] For example at 20° the photosensitised addition of maleic anhydride to *p*-xylene gave a 20:1 mixture of **30** and **31** respectively whereas at 100° this ratio changed to approximately 1:10 and thus it would seem that at the lower temperature 2,3-attack to give **32** is favoured but the 1,2-product **33** dominates the mixture at the higher temperature. However, reduction of the light intensity by 50% (Experimental) had a profound effect on the isomer distribution particularly in the case of the xylenes. Thus the two *p*-xylene isomers **30** and **31** were formed in a ratio of 1:10 at 20° and at 100° this was changed to 3:1 respectively. These data can be rationalised by a combination of the differing photo and thermal labilities of the precursor 1,2- and 2,3-*ortho* cycloadducts **33** and **32** respectively and their rates of thermal reaction with maleic anhydride. That is to say that it would appear that **32** adds maleic anhydride more readily than **33**, but is more thermally labile than **33** whereas **33** is photochemically more labile than **32**. Which of these features or their combinations has the greatest effect is not possible to determine but these data emphasise the importance of taking such aspects into consideration in the interpretation of the results from these systems.[15,28]



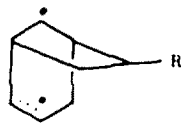
(32) $R=R^1=Me$, $R^2=R^3=H$

(33) $R^2=R^3=Me$, $R=R^1=H$

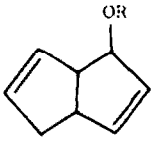
meta-*Photocycloaddition*

The *meta* photocycloaddition of ethylenes to arenes has been more systematically studied than the corresponding *ortho* process. Regioselectivities of the addition with respect to the arene have been interpreted in terms of both *meta* addition of the ethylene to the S_1 arene *via* an exciplex followed by formation of the ethenyl cyclopropane system,[6,7] and prior rearrangement of the arene to a "prefulvene" species which undergoes concerted ethylene addition.[9,22] The orientations of the substituents on the *meta* cycloadducts from some systems require that both mechanism operate in competition.[22] Determination of the regioselectivity of the addition with respect to an unsymmetrically substituted ethylene [i.e. 6- or 7-substituted **2**] would assist in

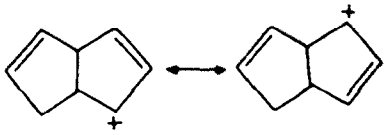
assessing the contribution from each of the above mechanisms in the overall pathway since the addition product **34** from the exciplex **7** may be expected to yield either regioisomers whereas dependent on the nature the ethylene substituent, one or other isomer would be favoured from such a species as **8**. The *meta* photocycloadditions of ethyl vinyl ether[10] and of vinyl acetate[29] to benzene have recently been described to be 60% regioselective towards the 7-*endo* isomers. Because of poor resolution of the isomers on preparative chromatography, the conclusion in the latter case was based largely on pyrolysis studies.[30] It is now reported that a more reproducible method of assessing the 6- and 7-regioselectivities of the *meta* adducts from vinyl acetate and arenes is the use of an acid catalysed elimination rearrangement reaction in the presence of alcohols to give 2-alkoxy bicyclo[3.3.0]octa-3,7-dienes (**35**). Refluxing the *meta* adduct mixture from benzene and vinyl acetate in acidified ethanol removed all isomers from the chromatogram and gave a 60% yield of the *exo* and *endo* stereoisomers of **36**. This process may arise by either acetate elimination to give semibullvalene which is known under such conditions to yield **36**,[31] or *via* an ethenyl cyclopropane assisted elimination from only the 7-regio isomers to the species **37** which then yields **36**. The low yields of **36** are in agreement with the latter



(34)



(35) R = alkyl
(36) R = C_2H_5
(37) R = C_2F_5



(37)

mechanism and suggest that the 6-isomers either decompose under these conditions or react by another route.[32] Support for a pathway not involving semibullvalene came from the observation that the product **35** from treatment of the acetate mixture with MeOD/DCl contained no deuterium: such an observation is consistent with the second mechanism. The reaction of 2,2,2-trifluoroethanol with the photoproduct in the absence of added acid substantiated the formation of **35** by the latter mechanism since the disappearance of the 7-isomers, monitored by capillary glc, was accompanied by concomitant formation of **38** and the 6-regioisomers and the *endo ortho* cycloadduct were recovered unchanged. By this reaction, the *meta* photocycloaddition of vinyl acetate to benzene is assessed to be 70% regioselective towards the 7-isomer and this suggests the involvement to some extent in the reaction pathway of a polar species such as **8**. Approximately 90% of the 7-regioisomers were stable under conditions for the thermal 1,5-sigmatropic shift rearrangement,[30] and hence it is deduced that the 7-*endo* acetate isomer of **2** accounts for some 63% of the total product: the 6-regioisomers were formed in equal amounts. Rates of formation of the *meta* cycloadducts were unaffected by solvent polarity but that of the *ortho* process was increased and it is also noteworthy that all vinyl acetate-benzene photoadducts were decomposed on benzene sensitised irradiation.

Irradiation of vinyl acetate with toluene produced a mixture of *meta* cycloadducts (M^+ = 178 m.u. MS/glc) and a very minor amount (*ca.* 5%) of a 1:1 adduct which had properties consistent with those of an *ortho* cycloadduct. 2,6-Regiospecific addition of the ethylene to toluene was confirmed (i.e. the Me group was specifically located on the 1-position of **2**) by ^{1}H NMR spectra of the adducts which thus suggests a route involving *meta* ethylene addition to the arene[6,7] rather than one of prior arene rearrangement.[22] Consistent with this interpretation, reaction of the *meta* adduct mixture with trifluoroethanol and pyrolysis studies as outlined above indicated little or no selectivity of the addition with respect to the ethylene.

The irradiation of vinyl acetate and anisole gave very similar results to those described above for toluene and this ethylene. Thus attack at the 2,6-positions of the arene accounted for approximately 90% of the total reaction mixture and the 7-regioisomers constituted some 50% of the *meta* cycloaddition.

These results and others with ethyl vinyl ether,[10] isobutene,[9] and methylene cyclobutane,[24] show that in the *meta* cycloaddition of ethylenes to benzene there is only limited regioselectivity and then only for ethylenes bearing a polar substituent: in this context the regiospecific *meta* addition of propene to benzene[23] is even more remarkable. The specificity for the formation of the 7-regio methyl isomers of **2** was deduced from the ^{1}H Me resonance positions of the two inseparable *meta* cycloadducts and their comparison with those of the but-2-ene-benzene adducts.[33] However, values in the literature for such resonances may span the range δ0.73–1.10 ppm for the 6-isomers and δ0.78–1.15 ppm for the 7-isomers and are very dependent on stereochemistry.[3,9,33] The isobutene-benzene *meta* addition shows little regioselectivity as the ratio of 7,7 to 6,6-dimethyl adducts was 1.25:1[9] but the reactant proportions in the two studies were quite different. In particular the latter system was studied as a 5% v/v solution of the ethylene in benzene and under such conditions the triplet yield of benzene would be high.[34] As noted above, *meta* cycloadducts are susceptible to benzene sensitised decomposition and thus the differing labilities of the adducts could account for the low regioselectivity in the isobutene addition. The benzene–isobutene system has been studied in isopentane solution at concentrations of the ethylene and arene comparable to those used earlier for the propene–benzene system. Under such conditions indeed the regioselectivity did increase but only to 1.6:1 for the 7- and 6-regioisomers respectively and the factors operating in the propene case which dictate the specific 7-addition remain obscure.

CONCLUSIONS

Preferred modes of cycloaddition of ethylenes to benzene and its substituted derivatives are largely predictable from electron donor–acceptor properties of the

addends. The present results concerning selectivities of *ortho* cycloadditions together with those we recently reported for ethenyl ether additions[10,11] show that there is no simple underlying feature which operates and controls the regio and stereo chemistries of this reaction. Some *ortho* cycloadducts are stereospecifically *exo* whereas in other cases both stereoisomers are formed. With substituted benzenes, attack of the ethylene at the arene 1,2-positions is generally favoured, the reaction is more selective with polar arene substituents than for alkyl benzenes, and solvent polarity can have a profound effect on regioselectivity but does not appear to influence the stereochemistry of the addition to any significant degree. Differing photolabilities of *ortho* cycloadducts and, in the case of maleic anhydride additions, their relative rates of reaction with dienophiles are important factors which must be considered for each system before selectivities of the process are reported.

By way of contrast, the selectivities of the *meta* photocycloaddition of ethylenes to arenes are high. The regioselectivity of the addition with respect to the arene can be understood in terms of two mechanistic pathways and for unsymmetrically substituted ethylenes there is evidence to suggest that formation of 7-substituted isomers are formed selectively in some cases. In general the *meta* cycloaddition favours *endo* stereochemistry.

EXPERIMENTAL

Irradiations of acrylonitrile, methacylonitrile, and vinyl acetate in the presence of the arenes were carried out in sealed quartz tubes using 15 watt low pressure mercury arc lamps. For preparative experiments equimolar amounts of the reactants (400 ml total amount) were irradiated for 24 hr at 20°. Solvent and time effects on isomer yields were examined using quartz tubes of 10 ml capacity in a motor-driven carousel arrangement adjacent to a 30 watt low pressure mercury arc lamp. Standard work-up procedure following hplc and/or glc analysis involved reactant removal under reduced pressure followed by vacuum distillation (0.05 mm Hg) of the yellow-orange oily residue. The 1:1 adducts were separated with varying degrees of success by flash chromatography over Kieselgel 60 (0.040–0.063 mm). The isolated adducts or their mixtures (0.5g) were treated with excess N-phenylmaleimide (1.0g) in diethyl ether (50 ml) and the system monitored by glc. The 1:1:1 adducts were filtered off and recrystallised from ethanol. In some cases formation of the Diels–Alder adducts was accelerated by refluxing the ether (4 hr) or similar treatment using EtOH (50 ml) as the solvent. Fractional crystallisation (EtOH) and/or flash chromatograph (Kieselgel 60) of the 1:1:1 adducts gave the isomers in >98% purity. In cases where the isomers (1:1 or 1:1:1 adducts) could be isolated essentially pure (hplc, tlc, and/or glc) they had satisfactory elemental analyses or accurate mass data.

Experiments involving maleic anhydride and the methylbenzenes were conducted in pyrex apparatus and employed one or two 500 watt medium pressure mercury arc lamps at the outside of the apparatus for "low" and "high" intensity irradiations respectively. The apparatus was water cooled or electrically heated to maintain the 20 or 100° reaction temps. In typical experiments solutions of maleic anhydride (10.0 g) and benzophenone (5.0 g) in the arene (150 ml) were irradiated for 6 hr. Standard work-up procedure involved removal of the methylbenzenes under reduced pressure and treatment of the semi-solid yellow residue with diethyl ether (200 ml). The crude solid product was filtered off and analysed by ^{1}H NMR spectroscopy in deuteriated dimethyl sulphoxide for isomer ratio estimation. The 2:1 regioisomers were isolated free from each other by repeat cycle fractional crystallisation from acetone: all had satisfactory elemental analyses and were assumed to have *exo endo* stereochemistries in view of the very close similarities of their spectroscopic properties with those of the 2:1 maleic anhydride benzene adduct of proven stereochemistry.

The *meta* cycloadducts could not be separated on a preparative scale into their regio and stereoisomers. The 7-regioisomers of the acetates were converted into 3$ derivatives by refluxing the soln of the adduct mixture (0.5 g) in either 2,2,2-trifluoroethanol (15 ml) or acidified (1 drop conc. HCl) in EtOH (15 ml).

The spectroscopic aspects of ethylene-arene photoadducts which allow structural assignments to be made have been presented in detail elsewhere[26] and so only features characteristic of the present adducts will be given in brief below: data given in the text is not reproduced here.

Acrylonitrile-arene 1:1 *adducts and* 1:1:1 *adducts with* N-*phenylmaleimide*

Compound **10**. ν_{max}(liquid smear) 2240 cm^{-1}, δ ($CDCl_3$), 2.46–2.75 (2H, m), 3.0–3.2 (1H, m), 3.38–3.55 (1H, m), 3.55–3.72 (1H, d of d, J's = 7Hz), 5.52–5.72 (2H, m), 5.72–5.88 (1H, m), and 5.98–6.12 ppm (1H, m).

Compound **11**. ν_{max}(liquid smear) 2240 cm^{-1}, δ ($CDCl_3$) 2.42–2.58 (1H, m), 2.58–2.90 (1H, m), 3.06–3.28 (1H, m), 3.28–3.52 (2H, m), 5.58–5.76 (2H, m), and 5.76–6.00 ppm (2H, m).

Compound **14**. M.p. 217–218°, ν_{max}(Nujol) 2220 and 1710 cm^{-1}, δ (($CDCl_3$), 1.88–2.08 (1H, m), 2.36–3.08 (6H, overlapping m's with s at 2.86 ppm), 3.31 (1H, br s), 3.42 (1H, br s), 6.38–6.60 (2H, m, 6 lines), 7.16–7.28 (2H, m), and 7.34–7.56 ppm (3H, m).

Compound **15**. M.p. 237–238°, ν_{max}(Nujol) 2220 and 1710 cm^{-1}, δ ($CDCl_3$), 1.88–2.06 (1H, m), 2.34–2.56 (1H, m), 2.64–2.98 (4H, m), 3.22–3.38 (2H, m), 3.48–3.60 (1H, m), 6.40–6.52 (1H, apparent t), 6.68–6.78 (1H, apparent t), 7.14–7.30 (2H, m), and 7.34–7.66 ppm (3H, m).

Compound **16**. ν_{max}(Nujol) 2220, 1710 cm^{-1}, δ ($CDCl_3$) 1.40–3.69 (12H, series of overlapping m's with two s at 2.17 and 2.20 ppm), 5.94–6.23 (1H, br d), and 7.00–7.66 ppm (5H, m). Major 1:1:1 adduct of toluene, acrylonitrile and N-phenylmaleimide, m.p. 216–217°, ν_{max} (Nujol) 2230 and 1710 cm^{-1} δ ($CDCl_3$) 1.45–3.50 (11H, series of overlapping m's with s at 1.52 ppm), 6.40–6.55 (2H, apparent t) and 7.15–7.70 ppm (5H, m); minor 1:1:1 adduct m.p. 192–196°, ν_{max} (Nujol) 2200 and 1710 cm^{-1}, δ values in $CDCl_3$ in text.

Compound **21**. M.p. 198–200°, ν_{max}(Nujol) 2220 and 1700 cm^{-1}, δ ($CDCl_3$) 1.33–3.93 (11H, overlapping m's with s at 3.32 ppm), 6.40–6.65 (2H, m), and 7.10–7.70 ppm (5H, m).

Methacrylonitrile-arene 1:1 *adducts and* 1:1:1 *adducts with* N-*phenylmaleimide*

Compounds **24** + **25**. ν_{max}(liquid smear) 2230 cm^{-1} δ ($CDCl_3$), 1.20–3.80 (7H, overlapping m's with two s at 1.56 and 1.61 ppm), and 5.25–6.25 ppm (4H, m).

Compound **26**. M.p. 231°, ν_{max}(Nujol) 2220 and 1705 cm^{-1}, δ ($CDCl_3$) 1.34 (3H, s), 1.45–2.00 (2H, m), 2.38–3.64 (6H, m), 6.20–6.60 (2H, br quintet), 7.08–7.31 (2H, m), and 7.31–7.60 ppm (3H, m).

Compound **27**. M.p. 186°, ν_{max}(Nujol) 2227 and 1710 cm^{-1}, δ ($CDCl_3$) 1.54 (3H, s), 1.65–3.65 (8H, overlapping m's), 6.25–6.55 (1H, br apparent t), 6.55–6.82 (1H, br apparent t), 7.05–7.31 (2H, m), and 7.31–7.60 ppm (3H, m).

Minor 1:1:1 adduct from anisole and methacrylonitrile δ ($CDCl_3$) 1.44–3.62 (8H, overlapping m's), 1.60 (3H, s), 3.66 (3H, s), 4.83–5.12 (1H, d of d), and 7.00–7.60 ppm (5H, m), major 1:1:1 adduct 1.43 and 1.59 (total 3H, two s), 3.14 and 3.46 (total 3H, two s), 2.00–4.20 (7H overlapping m's), 6.22–6.80 (2H, m) and 7.00–7.60 ppm (5H, m).

Maleic anhydride-toluene 2:1 *adducts*

Compound **30**. M.p. 255–257°, ν_{max}(Nujol) 1852 and 1781 cm^{-1} δ (deuteriated dimethyl sulphoxide) 1.42 (6H, s), 2.20–3.23 (6H m's with s at 3.03 ppm), and 6.13 ppm (2H, s).

Compound **31**. M.p. > 330°, ν_{max}(Nujol) 1852 and 1780 cm^{-1} δ (deuteriated dimethyl sulphoxide) 1.10 (3H, s), 1.73–1.93 (3H, d, J = 2Hz), 2.33–3.50 (7H, m's), and 6.03–6.25 ppm (1H, m).

Vinyl acetate–arene adducts

Benzonitrile major adduct. ν_{max} (liquid smear) 2220 and 1735 cm^{-1}, δ ($CDCl_3$) 1.80–2.80 (4H, m's), 2.13 (3H, s), 5.66–6.34

(3H, m) and 6.70–6.95 ppm, (1H, m). N-Phenylmaleimide derivative, m.p. 216–218°C, ν_{max}(Nujol) 2235, 1745, 1715 cm^{-1}, δ ($CDCl_3$), 1.94–2.12 (1H, m), 2.16 (3H, s), 2.38–2.58 (1H, m), 2.80–2.94 (1H, m), 2.98–3.10 (1H, m), 3.30–3.50 (2H overlapping m's), 3.72–3.84 (1H, m), 4.52–4.68 (1H, dd), 6.40–6.60 (2H, m), 7.10–7.30 (2H, m), and 7.30–7.55 ppm (3H, m).

1:1 *Minor adduct*. ν_{max} (liquid smear) 2220 and 1735 cm^{-1}, δ ($CDCl_3$) 1.80–3.60 (4H, overlapping m's), 2.00 (3H, s), 5.35–5.80 (3H, 3 br lines), and 6.55–6.70 ppm (1H, br d).

Essential features of the IR and ^{1}H NMR spectra of the adducts mixtures from vinyl acetate with benzene, toluene, and anisole are given in reference 29.

Isobutene–benzene

A soln of benzene (10 ml), isobutene (20 g) in isopentane (40 ml) was irradiated at 5° for 8 hr using a 6 watt low pressure mercury arc immersion lamp. The starting materials were removed under reduced pressure and the adduct mixture was analysed and separated as described in Ref. 9.

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