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PHOTOCYCLOADDITION OF ETHENES TO CYANOANISOLES

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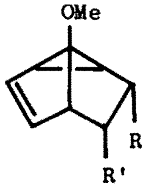
Abstract - The photoreactions of 2-,3-, and 4-cyanoanisole with cis cyclo-octene, ethyl vinyl ether and acrylonitrile have been investigated. Additions of the cyclo-alkene reflect control of the reaction by the methoxy group to give predominantly meta cycloadducts by 2,6-attack. In contrast these arenes and ethyl vinyl ether undergo ortho cycloaddition which in the case of the product from the 2-arene isomer, leads to a convenient high yield synthesis of the bicyclo[4.2.0]octa-2,7-diene (23). The reactions of acrylonitrile with 2- and 3-cyanoanisoles are slow and non-selective but ortho cycloadducts are formed from the 4-isomer which also undergoes novel photoaddition with the cyano group of both acrylonitrile and benzonitrile to give azacyclo-octatetraenes.

There are numerous publications describing the photocycloaddition reactions of a wide variety of ethenes to benzenoid compounds which have either electron donor or electron acceptor substituents.[1] The literature concerning mechanistic aspects of these processes is extensive,[2-7] and the preferred mode of cycloaddition is now predictable and is dependent on the electron donor-acceptor relationships of the addends.[3,6] For example, acrylonitrile undergoes 1,2-addition to anisole[8] whereas cycloalkenes[9] and enol ethers[10] yield meta cycloadducts (1) by 2,6-addition with this arene. The most efficient addition reactions of such ethenes to benzonitrile, however, occur by attack at the nitrile functionality to yield azetines and 2-aza-1,4-butadienes and/or ortho cycloaddition at the nucleus to give bicyclo[4.2.0]octa-2,4-dienes.[11] The only example where meta cycloaddition to benzonitrile is the preferred pathway has trans 1,2-dichloroethene as the addend and in this case it appears that a 2,4-alignment with respect to the arene is favoured by steric and/or polarity factors.[12] In contrast to this wealth of data, information concerning the excited state chemistry of benzenoid compounds having both electron donor and electron acceptor substituents is sparse. Indeed no photoadditions of ethenes to such arenes were reported until 1985 when the preliminary accounts of meta cycloaddition of cyclopentene to 3- and 4-cyananisole[13] and of the present study[14] were published.

The previous lack of interest in these benzenoid compounds may have reflected an assumption that, at least for the 2- and 4-isomers, the lowest excited state would be predominantly of charge-transfer character[15] and not the $S_1\pi\pi^*$ excited benzene ring which is responsible for the cycloaddition processes. The relative



(1)

R-R' = $-(CH_2)_n-$
R=H, R' = -O-alkyl
R = -O-alkyl, R'=H
R-R' = $-(CH_2)_2-O-$ or $-O-(CH_2)_2-$

levels of the states are dependent on the position of the substituents.[16,17] Thus while the absorption spectra of the 2- and 3-cyanoanisoles are very similar having the ^1L_b-related band in the 280-310 nm region [ε(methylcyclohexane) = ca. 4 and 3 x 10^3 $M^{-1}cm^{-1}$ respectively] and the ^1L_a-related band ("intramolecular charge-transfer bands at $\lambda < 240$ nm, they are markedly different from that of the 4-isomer which has only weak absorption at 265-295 nm for the former transition but an intense absorption with λ_{max} 245 nm (ε = ca. 16 x 10^3 $M^{-1}cm^{-1}$) for the latter band.[16] We have observed that the photolabilities of these arenes in the presence of ethenes vary appreciably and we now report details of the diverse photocycloaddition reactions which result from these systems. The novel formation of azacyclo-octatetraenes by the first reported examples of photocycloaddition of a nitrile group to an aromatic nucleus and of a facile high yield synthesis of bicyclo[4.2.0]octa-2,7-dienes are also described.

Results and Discussion

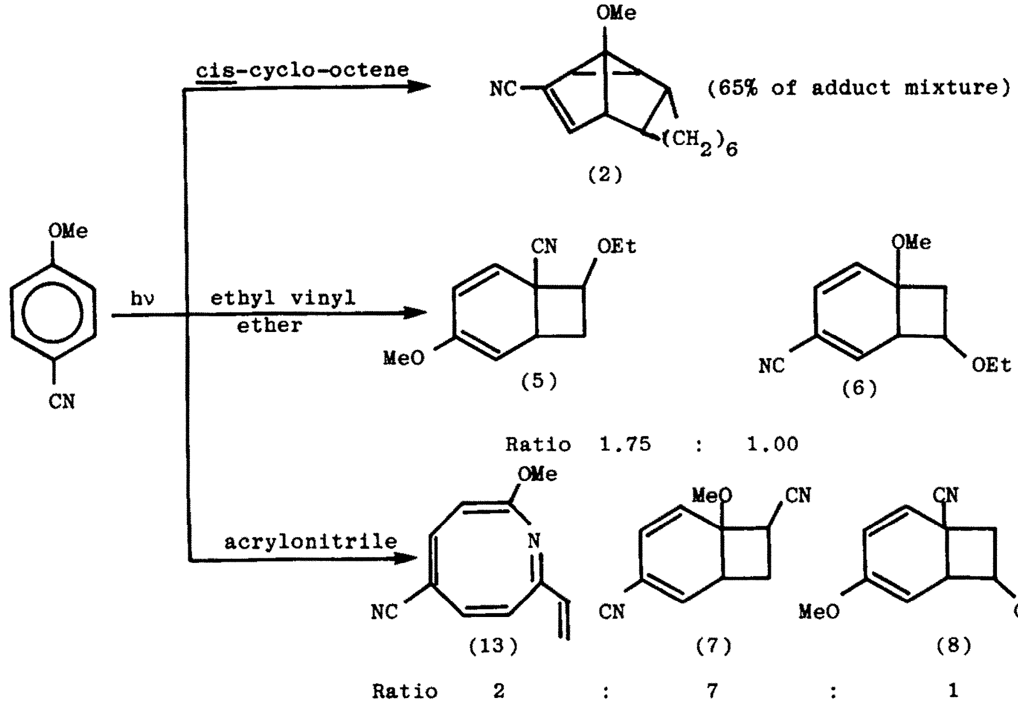
Preliminary examination of the 254 nm irradiation of the three cyanoanisoles in the presence of ethenes of varying electron donor and acceptor capabilities revealed that the 4-isomer was the most reactive and readily gave mixtures of 1:1 adducts. The photoreactions of the 2- and 3-isomers were generally less efficient and for some systems gave complex mixtures in low chemical yields. The reactions of the arenes were studied in detail with cis cyclo-octene, ethyl vinyl ether and acrylonitrile since the photoreactions of these ethenes with benzene, anisole, and benzonitrile are well-documented.[1,2] For preparative purposes, solutions of the arene (0.2M) in neat ethene were irradiated at 254 nm under nitrogen and the reaction monitored chromatographically (TLC and GC). Products were isolated by flash chromatography and the structures were assigned principally from the ^{1}H n.m.r. spectra and their comparison with the extensive published data for the ortho and meta cycloadducts of ethenes and arenes.[1,18]

4-Cyanoanisole

The major products from the reactions of 4-cyanoanisole with the above ethenes are summarised in the Scheme.

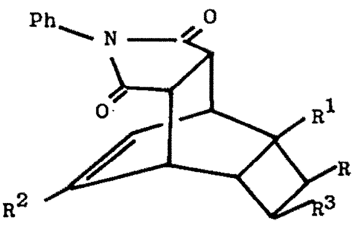
Consistent with the recent findings of Cornelisse et al. for the photoaddition of cyclopentene to 4-cyanoanisole,[18] the major product from the irradiation of this arene with cis cyclo-octene was the endo meta cycloadduct (2) which arises from 2,6- addition of the ethene to the anisole. Isomeric cycloadducts are formed but (2) comprised 65% of the reaction mixture (cf. 45% of this isomer from cyclopentene[18]) at 50% arene conversion in neat ethene or using non-polar solvents as diluents. Irradiations in acetonitrile or methanol did not affect the rate of formation of (2) but did produce an enhancement of a previously minor 1:1 adduct (9% in ethyl acetate) to a respective 3:5 ratio with (2). This minor product reacted quantitatively with N-phenylmaleimide and although the ^{1}H n.m.r. spectra of both the 1:1 adduct and its Diels-Alder product provided evidence for the presence of three isomers from the ortho cycloaddition reaction in approximately equal amounts, neither mixture could be separated chromatographically into the pure components. The marked enhancement

Scheme Major 1:1 Adducts formed between 4-Cyanoanisole and Ethenes



in the efficiency of this 4-cyanoanisole-cyclo-octene reaction on increase in solvent polarity is characteristic of an ortho cycloaddition process.[19]

The reaction mixture from irradiation of ethyl vinyl ether and 4-cyanoanisole was complex on prolonged irradiation (twelve 1:1 adduct isomers) but two major adducts (ratio ca. 1:1.75 increasing GC retention times on non polar columns) together comprising approximately 70% were formed at <50% arene conversion. These 1:1 adducts reacted readily with N-phenylmaleimide and were best isolated and separated as their Diels-Alder adducts. From the structural assignments of (3) and (4) to these 1:1:1 adducts, the major and minor photoadduct isomers were deduced to be (5) and (6) respectively. The rates of formation of the ortho cycloadducts (5) and (6) and three of the minor products were increased by four-fold on change of solvent from cyclohexane to acetonitrile. Although as noted above this feature is typical of the ortho cycloaddition reaction,[19] it is to be noted that the 2,6-(meta) cycloaddition of ethyl vinyl ether to anisole has been shown to be similarly enhanced[10a] and hence the solvent effects on the formation of the minor reaction components in the present mixture do not distinguish between the two modes of reaction.

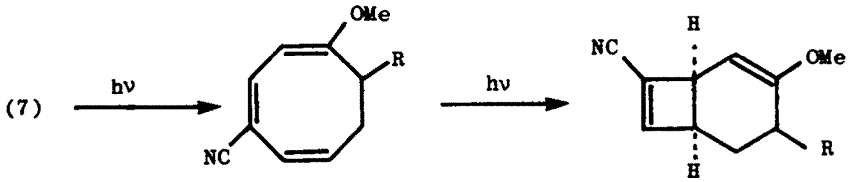


(3) R=OEt, R^1=CN, R^2=OMe, R^3=H
(4) R=H, R^1=OMe, R^2=CN, R^3=OEt
(9) R=CN, R^1=OMe, R^2=CN, R^3=H
(10) R=H, R^1=CN, R^2=OMe, R^3=CN

Both cis cyclo-octene[20] and ethyl vinyl ether[10] undergo 2,6- (meta) photocycloaddition to anisole essentially exclusively whereas their major reaction with benzonitrile involves 1,2 (ortho) cycloaddition.[10,21] In view of the closely similar electron donor properties of these ethenes as judged by ionisation potentials, their same mode of reaction with a particular arene may have been expected,[22] and on this basis it appears surprising that the major photoreactions of the cyclo-alkene and the enol ether with 4-cyanoanisole should result from different pathways. In the former case the addition to 4-cyanoanisole in non-polar solvents is largely controlled by the methoxy substituent giving the 2,6-(meta) adduct (2), whereas for ethyl vinyl ether the major mode of reaction reflects the cyano group exerting the stronger influence to promote the ortho cycloaddition. It is, however, noteworthy that while the formation of (5) may be expected, the 1,2-addition of the enol ether to cyanoanisole giving (6), is unprecedented. Further, it is of particular interest that the present preference for meta cycloaddition of cis cyclo-octene and ortho cycloaddition of ethyl vinyl ether has also been observed between these ethenes and benzene.[12,23] For additions to benzene, there is a satisfying correlation between the favoured modes of cycloaddition and the free enthalpies of electron transfer.[3,5] This predictive treatment may be generally applicable to the reactions of benzene derivatives in non-polar solvents but steric and polarity features of addend substituents which are likely to influence the orientation of the molecules in intermediates also require careful consideration. We have already discussed the role allylic $-CH_2-$'s play in determining the alignment of addends for meta cycloaddition[4] and for cis cyclo-octene, this "intermolecular hyperconjugation" feature, which is absent from ethyl vinyl ether, may be sufficient to favour the 2,6-addition to 4-cyanoanisole. On the other hand, the polarised ethene bond of enol ethers may be expected to align in a parallel orientation with similar features in the arene C-C bonds and this would lead to ortho cycloaddition.

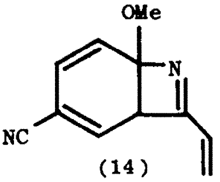
Acrylonitrile undergoes 1,2-cycloaddition both to anisole[8] and less readily to benzonitrile[24] so the formation of (7) and (8) in a respective ratio of 7:1 (60% conversion of arene) from this ethene and 4-cyanoanisole is not unexpected. These adducts were isolated and separated as their Diels-Alder N-phenylmaleimide adducts (9) and (10) respectively. Both photoadducts were formed more efficiently in acetonitrile than in cyclohexane solvent and both were photolabile. The product from irradiation of (7) was the cyclo-octatriene (11) which was the major product following irradiation of the 4-cyanoanisole-acrylonitrile system to complete conversion of the starting arene. During isolation of the triene (11) by flash chromatography from prolonged irradiation experiments, the presence of a further 1:1 adduct (M^+ = 186 m.u. MS/GC) was revealed in the fractions. This isomer comprised <5% of the total adduct mixture and could not be completely freed from (11) but from the ^1H n.m.r. spectrum of samples of 90% purity, the bicyclo[4.2.0]octa-2,7-diene structure (12) was tentatively assigned. This adduct isomer was shown to arise by a secondary photoreaction from the cyclo-octatriene (11) but compared to the other photoisomerisations of this type which were observed in this study the conversion of (11) to (12) has a very low efficiency.

The third 1:1 adduct of acrylonitrile and 4-cyanoanisole had the lowest chromatographic retention properties of the products, constituted 20% of the reaction mixture and was isolated as orange crystals (m.p. 55-56°C). The ^1H n.m.r. spectrum of this adduct showed the presence of only ethenyl (7H δ 6.80-5.32) and methoxy (δ 3.88) protons, and from the spectroscopic properties of this adduct, the azacyclo-octetraene structure (13) was assigned:

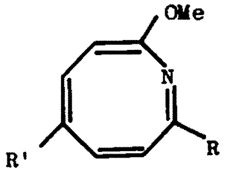


(11) R=CN
(18) R=CH_2CN

(12) R=CN
(17) R=CH_2CN



(14)



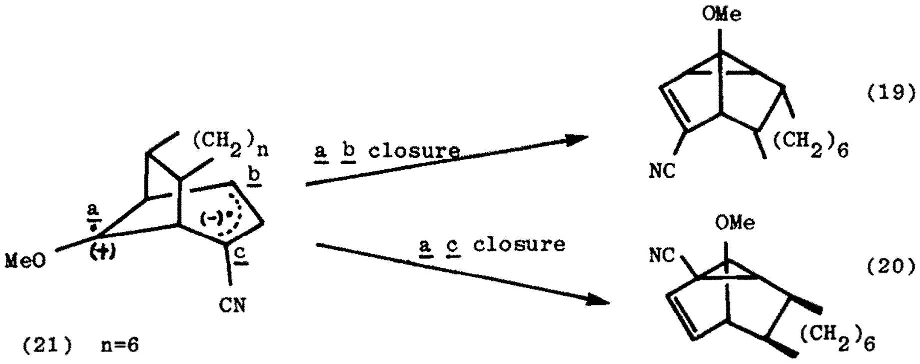
(15) R=Ph, R'=CN
(16) R=$-CH=CH_2$, R'=CO_2Me

this was confirmed from an X-ray crystallographic determination of a single crystal.[14] Although the photoaddition of acetylenes to benzenes to give cyclooctatetraenes is a well-documented process,[1] the formation of (13) represents the first example of the photoaddition of a nitrile to an arene. The presumed precursor, 7-azabicyclo[4.2.0]octa-2,4,7-triene (14), of (13) was not detected in the present reaction and experiments with other benzenoid compounds and nitriles revealed that there are particular requirements for this type of cycloaddition to occur. Thus photoaddition of the nitrile group to the benzene ring was not observed from irradiation of acrylonitrile in the presence of benzonitrile, anisole or the 2- and 3-cyanoanisoles and furthermore no such product was obtained from acetonitrile and 4-cyanoanisole. On the other hand, irradiation of 4-cyanoanisole in the presence of benzonitrile gave only one product (TLC) which was isolated as orange crystals (m.p. 94-96°C) and assigned the azacyclo-octatetraene structure (15). Further, a minor product (m.p. 38-40°C) in the reaction mixture from irradiation of acrylonitrile and *p*-methoxy methyl benzoate was shown from its spectroscopic properties and their comparison with those of (13) to be the carbomethoxy azacyclo-octatetraene (16). It is thus evident that the nitrile addition to the benzene ring only occurs for arenes having electron donor and electron acceptor groups in a *para* relationship and for nitriles which are conjugated. The latter feature may indicate that excitation of the nitrile is necessary for the photoaddition. However, from a study of the effect of addend concentration on the formation of (13), it is deduced that the photoexcited 4-cyanoanisole is the species fruitful of reaction: efficient quenching of the arene fluorescence by acrylonitrile was also observed. The role of the addend substituents in the formation of (13) may be to align the nitrile group and the benzene ring in the particular orientation required for the 1,2-addition process (*cf*. suggested addend orientations in the proposed intermediate exciplexes for the addition of aryl nitriles to ethenes[11]): no evidence was, however, obtained from UV absorption or fluorescence spectroscopy for the presence of either ground state or excited state complexation between the addends.

While assessing the influence of the nitrile structure on the formation of the azacyclo-octetraenes, we also examined the 4-cyanoanisole-allyl cyanide system. Irradiation of solutions of the arene in allyl cyanide very slowly produced three 1:1 adducts (M^+ = 300 m.u. MS/GC) in a ratio which varied appreciably with the degree of arene conversion (*e.g.* 1.5 : 2 : 3 at 5% conversion). The two isomers of shortest retention time had a low photostationary concentration and from preparative experiments constituted <10% of the reaction mixture. On flash chromatography the two minor isomers decomposed but the major 1:1 adduct was isolated in >99% purity (GC). The ^1H n.m.r. spectrum showed the presence of two ethenyl protons, one shielded (δ 4.86) and one deshielded (δ 6.86) and detailed spectral analysis of this product allowed the bicyclo[4.2.0]octa-2,7-diene structure (17) to be assigned. The formation of (17) is again rationalised by a secondary photoprocess involving the cyclooctatriene isomer (18) which is the photochemical and/or thermal product of the primary *ortho* photocycloadduct.[25] Although neither of the latter two isomers was isolated, it is evident that the rearrangements to give (17) are considerably more efficient than that observed for (12) but still the chemical yields of (17) are lower than those attained from the addition of ethyl vinyl ether to 2-cyanoanisole (see below).

2- and 3-Cyanoanisoles

Irradiation of both arene isomers in the presence of acrylonitrile and of *cis* cyclo-octene with 2-cyanoanisole gave low chemical yields of multi-component mixtures in which no one component constituted greater than 15%. In contrast, irradiation of 3-cyanoanisole in the neat cyclo-alkene readily gave two 1:1 adducts (M^+ = 243 m.u.) in a time invariant ratio of 1.0:1.4 (order of retention time on non polar GC columns). These isomers were isolated by flash chromatography and from their ^1H n.m.r. spectra and their comparison with those of the *meta* cycloadducts of this arene and cyclopentene,[18] the minor and major adducts are respectively assigned structures (19) and (20) which are considered to arise from the two modes of cyclopropane formation in the intermediate (21).[26] The corresponding adducts with cyclopentene as addend are formed in approximately equal amounts in cyclohexane whereas that analogous to (19) is greatly favoured in polar solvents (5.15:1). In contrast the effects of solvent on the addition of *cis* cyclo-octene are weak and the respective ratios of (19) and (20) only vary from 1.0 : 1.4 in cyclohexane to 1.0 : 1.2 in methanol. The enhanced *a b* cyclisation in (22) with cyclopentene as the addend has been interpreted in terms of a higher negative charge at the unsubstituted carbon of the allylic moiety resulting from its greater accessibility towards polar solvents.[18] In the intermediate (21) from *cis* cyclo-octene, molecular models suggest that the "floppy" nature of the hexane bridge may impose a steric constraint on this effect and account for the reduced influence of solvent on the selectivity of the cyclopropane formation.

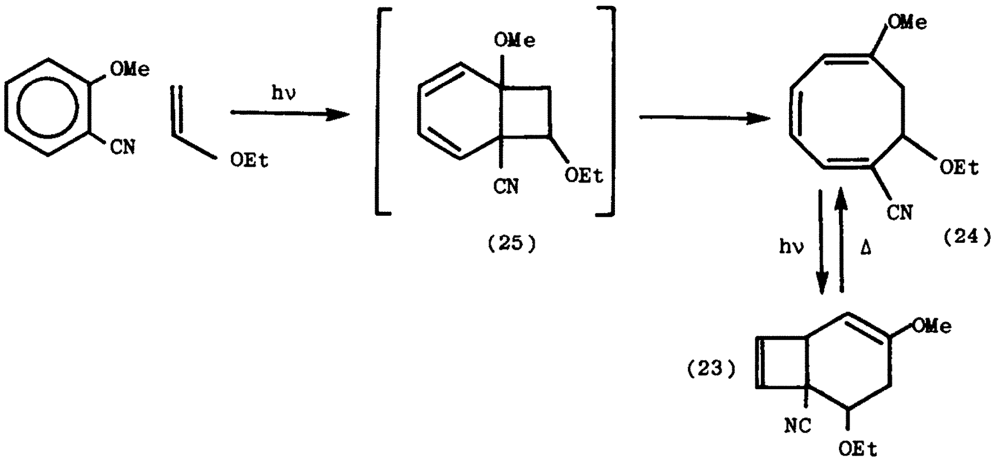


(21) n=6

(22) n=3

3-Cyanoanisole reacted very slowly with ethyl vinyl ether photochemically to give twelve products. At arene conversions <10%, two 1:1 adducts (M^+ = 243 m.u. ratio 1:1) comprised approximately 60% of this mixture but both were photolabile and reached a photostationary ratio and combined concentration of the total products of 1:2 (order of GC elution on non polar columns) and 40% respectively. Conversions of arene above 30% were strongly inhibited by radiation absorbing products in solution and as a result of this and the mixture complexity, it was impractical to isolate these photoadducts. Both isomers, however, readily fragmented to starting materials on electron impact (MS/GC)[27] and were completely removed from the product chromatogram by refluxing the mixture with N-phenylmaleimide in ethanol: from these features it is deduced that the two major products arise by ortho cycloaddition of the enol ether to the arene to give bicyclo[4.2.0]oct-2,4-diene derivatives but neither of the Diels Alder adduct isomers was isolated with sufficient purity to render spectroscopic analysis meaningful.

In contrast to the 3- and 4-cyanoanisoles, the irradiation of the 2-arene isomer with ethyl vinyl ether led to a specific cycloaddition reaction and the facile synthesis of a bicyclo[4.2.0]octa-2,7-diene. At low arene conversions (<1%) two 1:1 adducts (M^+ = 205 m.u.) were evident but as the reaction proceeded this ratio changed rapidly to favour greatly the isomer of lower retention time on GC non-polar columns until at 30% conversion of the arene, the ratio was 15:1 and when the arene had completely reacted, the minor component comprised <2% of the product mixture. Similar results were observed from solutions of the arene in ethyl vinyl ether in pyrex tubes exposed to sunlight and both here and with 254 nm irradiation, the reaction rate was increased approximately two-fold by change of the solvent from cyclohexane to acetonitrile. The major adduct isomer was obtained with 95% purity in 90% yield by vacuum distillation of the reaction mixture and freed from the minor component by flash chromatography. Spectral data allowed the assignment of a bicyclo[4.2.0]octa-2,7-diene structure to this photostable isomer (m.p. 27-29°C) and most surprisingly were consistent with the formation of essentially only one [i.e. (23)] of the two possible diastereoisomers. Why one disrotatory closure in the cyclo-octatriene precursor of (23) should be so greatly favoured over the other is not evident but it is noteworthy that the other two bicyclo[4.2.0]oct-2,7-dienes reported here also appear to be predominantly one isomer. Heating (23) at 180°C yielded much polymer and a yellow 1:1 adduct isomer which was readily converted back to (23) by 254 nm radiation and which had identical chromatographic properties to those of the photolabile isomer produced during the photoaddition reaction. The photolabile adduct was assigned the cyclo-octatriene structure (24) from its spectral data, and its formation during the photoaddition of 2-cyanoanisole to ethyl vinyl ether was established by spectroscopic examination of reactions at low arene conversions. The logical precursor of (24) is the ortho cycloadduct (25) but this isomer was detected neither spectroscopically nor chromatographically during the photoaddition reaction and attempts to trap (25) as a Diels Alder adduct were unsuccessful. The high lability of (25) may result from the steric crowding of the substituents facilitating the ring opening reaction to (24): certainly the formation of the triene is very rapid since its presence was readily detected by absorption spectroscopy in reactant solutions after only 5 min. exposure to a 6 w. low pressure mercury arc lamp. Formation of the bicyclo[4.2.0]octa-2,7-diene (23) by this "one-pot" photochemical route is very convenient and occurs in good yields from readily available starting materials and hence this method should provide an attractive direct access to such systems.



To summarise, the photoadditions of the cyanoanisoles to cis cyclo-octene, ethyl vinyl ether, and acrylonitrile show considerable variation in reaction modes and, particularly, in reaction efficiencies. For example, only 4-cyanoanisole photoadds with any degree of efficiency and selectivity to acrylonitrile and the 2-arene isomer is relatively unreactive except in the presence of the enol ether when a specific high yielding addition occurs to give ultimately a bicyclo[4.2.0]octa-2,7-diene. Nevertheless there are some consistent features within these systems. Thus the cycloalkene additions occur predominantly by a 2,6-(meta) attack with respect to the methoxy group and hence directly parallel the additions to anisole rather than to benzonitrile: that is to say the methoxy group is the directing influence. In marked contrast, the reactions of the enol ether with the cyanoanisoles all arise from ortho cycloaddition and hence reflect that control of the reaction mode is by the benzonitrile rather than the anisole moiety.

Experimental

Irradiations of 0.2M solutions of the arenes in neat ethenes were carried out in 50x1cm silica tubes under nitrogen using two 60 cm 30w low pressure mercury arc lamps. The study of solvent effects on reactions used 10x1cm quartz tubes in a "merry-go-round" apparatus holding eight such tubes with the arene (0.2M) and the ethene (2.0M) in cyclohexane, ethyl acetate, methanol and acetonitrile: the radiation source comprised two 8 cm 6w low pressure mercury arc lamps and 2,2,4,4,6,8,8-heptamethylnonane was used as the internal standard. Reactions were monitored by TLC with Camlab Polygram G/U.V. and mixtures of diethyl ether and 30-40^{o} b.p. petroleum ether as the eluent, and by gas chromatography on a Hewlett Packard 5790A instrument fitted with a flame ionisation detector and a 12m BP1 (OV1 equivalent) bonded phase capillary column.

The standard work-up procedure of reactions involved reactant (and solvent) removal by rotary evaporation, distillation of the crude mixture at 0.05 mm Hg pressure and separation of the products by flash chromatography on Silica Woelm 32-63 with mixtures of diethyl ether and 30-40^{o} b.p. petroleum ether as eluent. The Diels-Alder adducts of the ortho photocycloadducts were prepared by refluxing the vacuum distilled reaction mixture (0.3g) in ethanol or toluene (15 ml) with N-phenylmaleimide (0.3g) until the photoadducts were no longer evident by TLC and GC. The solvent was removed by rotary evaporation and diethyl ether (30 ml) added to the residue. The insoluble crude Diels-Alder adducts were filtered off and subjected to flash chromatography. The data which allowed structural assignments to be made for the adducts obtained by the above procedures are given below.

4-Cyanoanisole

The *meta* photoadduct (2) was isolated in >99% purity (GC; TLC one spot) using 3:5 v/v mixture of diethyl ether and the petroleum ether as eluting solvent. δ (CDCl$_3$) 6.64 (1H, dd, J's = 3 and 1.5Hz), 3.42 (3H,s), 3.28 (1H, m, J's = 6 and 3Hz with minor couplings), 2.82 (1H, m, J's = 6 and 3Hz with minor couplings), 2.66 (1H, dd, J's = 7 and 3Hz), 2.55 (1H, overlapping dd, J's = 7 and 7Hz), 2.28 (1H, dd, J's = 7 and 1.5Hz) and 1.7-1.1 (12H, overlapping m's); ν_{max} (Nujol) 2220 cm^{-1}; M^+, calc. 243.1618, found m/z 243.1617. Irradiation of these addends in methanol solution produced two 1:1 adducts (M^+ = 243 m.u. GC/MS) in a ratio of 3:5 and with respective relative retention times on GC of 0.9:1.0. The minor adduct was resolved neither by TLC nor GC but the ^{1}H n.m.r. showed three methoxy singlets in the 3.5-3.0 p.p.m. region and the N-phenylmaleimide reaction product of the photoadduct mixture had three singlets in the 3.7-3.4 p.p.m. region (ratio 1:1:1): this Diels Alder adduct also could not be resolved chromatographically.

The two *ortho* cycloadducts (5) and (6) (respective ratio 1.75:1.00, M^+ = 205 m.u. GC/MS) of 4-cyanoanisole and ethyl vinyl ether were best separated as their Diels Alder adducts with N-phenylmaleimide: this was achieved in refluxing toluene. The major adduct (5) reacted more rapidly than (6) and its N-phenylmaleimide adduct (m.p. 169-171°C) (3) was isolated by cooling the reactant solution when its presence was no longer evident by GC. δ(CDCl$_3$) 7.50-7.30(3H,m), 7.30-7.15 (2H,m), 4.88 (1H, dd), 3.72 (1H, dd), 3.56 (3H,s), 3.50-3.15 (5H,m), 3.08 (1H,dd), 3.00-2.75 (1H,m), 2.50-2.15 (1H,m), 2.05-1.70 (1H,m), and 1.25 (3H,t). ν_{max} (Nujol) 2240 cm^{-1}; M^+ calc. 378.1574, found m/z 378.1595. (4) was isolated by flash chromatography but was persistently contaminated with 4-5% of (3) (HPLC). δ(CDCl$_3$) 7.60-7.45 (3H,m), 7.38 (1H,dd), 7.30-7.20 (2H,m), 3.95 (1H,dd), 3.85-3.60 (2H, overlapping dd and m), 3.60-3.40 (3H, overlapping dd and q), 3.35 (3H,s), 3.15 (1H,dd) and 2.8-2.5(2H,m). ν_{max} (Nujol) 2220 cm^{-1}.

The three 1:1 adducts (M^+ = 186 m.u. GC/MS) of acrylonitrile and *p*-cyanoanisole were formed in an initial ratio 2:7:1 with respective relative GC retention times of 1:1.85:2.20. The latter two reacted readily in refluxing ethanol with N-phenylmaleimide and were best isolated and separated as their Diels-Alder derivatives (9) and (10) respectively. (9),(m.p. 233-235°C), δ(CDCl$_3$) 7.56 (3H,m), 7.48 (1H,dd), 7.28 (2H,m), 4.00 (1H,dd), 3.63 (1H,br.s), 3.46 (1H,dd), 3.38 (3H,s), 3.34 (1H,dd), 3.18 (1H,dd), 2.59 (2H,m), and 1.60 (1H,m). ν_{max} (Nujol) 2240 and 2220 cm^{-1}; M^+ calc. 359.1266, found m/z 359.1268. (10), m.p. 356-358°C, δ(CDCl$_3$) 7.54 (3H,m), 7.24 (2H,m), 5.08 (1H,dd), 3.72 (3H,s), 3.67 (1H,dd), 3.59 (1H,dd), 3.45 (2H,m), 3.22 (1H,dd), 3.12 (1H,dd), 2.90 (1H,t), and 2.55 (1H,dd). ν_{max} (Nujol) 2240 cm^{-1}; M^+ calc. 359.1266, found m/z 359.1269. The shortest retention time product was the azacyclo-octatetraene (13), m.p. 54-56°C, δ(CDCl$_3$) 6.80 (1H,d), 6.49 (1H,dd), 6.24 (1H,d), 6.08 (1H,d), 5.55 (1H,dd), 5.32 (1H,d), and 3.88 (3H,s); ν_{max} (smear) 2220 cm^{-1}; M^+ calc. 186.0791, found m/z 186.0806. Prolonged irradiation of this system gave (13) and the cyclo-octriene (11): the latter had δ(CDCl$_3$) 6.67 (1H,d), 6.33 (1H,d), 6.05 (1H,m), 5.90 (1H,dd), 3.86 (3H,s), 2.93 (1H,dd), 2.60 (1H,m), and 2.20 (1H,m); ν_{max} (smear) 2240 and 2220 cm^{-1}; M^+ calc. 186.0791, found m/z 186.0796. The following spectral features were obtained from 90% pure samples of the bicyclo[4.2.0]octa-2,7-diene (12), δ(CDCl$_3$) 6.61 (1H, br.s), 4.92 (1H,dd), 3.82 (1H,t), 3.69 (3H,s), 3.36 (1H,m), 3.26 (1H,m), 2.19 (1H,m), and 2.06 (1H,m); ν_{max} (smear) 2240 and 2220 cm^{-1}; M^+ 186 mu (GC/MS).

Irradiation of 4-cyanoanisole (1M) and benzonitrile (1M) in ethyl acetate for 3 days gave (15) (m.p. 94-96°C) as the sole product. δ(CDCl$_3$), 7.70-7.17 (5H,m), 6.76 (1H,d), 5.60 (1H,d), 6.07 (2H,dd), and 3.83 (3H,s). M$^+$ calc. 236.0947, found m/z 236.0939.

The bicyclo[4.2.0]octa-2,7-diene (17) from 4-cyanoanisole and allyl cyanide was an oil with δ(CDCl$_3$) 6.86 (1H,br.s), 4.86 (1H,dd), 3.78 (1H, overlapping dd), 3.60 (3H,s), 3.34 (1H,m), 2.43 (1H,m), 2.18 (1H,m), and 1.68 (1H,m); ν_{max} (smear) 2240 and 2220 cm^{-1}; M$^+$ calc. 200.0947, found m/z 200.0956.

3-Cyanoanisole-*cis* Cyclo-octene

The 1:1 *meta* cycloadducts were separated by flash chromatography. (19) δ(CDCl$_3$) 6.70 (1H,dd), 3.52 (1H,m), 3.38 (3H,s), 3.28 (1H,m), 2.96 (1H,m), 2.78 (1H,m), 2.12 (1H,dd), and 1.85-1.05 (12H, overlapping m's); ν_{max} 2220 cm^{-1}; M$^+$ calc. 243.1618, found m/z 243.1628. (20) δ(CDCl$_3$) 5.79 (1H,dd), 5.71 (1H,d), 3.62 (1H,m), 3.52 (3H,s), 3.22 (1H,m), 2.78 (1H,m), 2.63 (1H,m), and 1.85-1.05 (12H, overlapping m's); ν_{max} 2240 cm^{-1}; M$^+$ calc. 243.1618, found m/z 243.1631.

2-Cyanoanisole-Ethyl vinyl ether

The ^{1}H and ^{13}C n.m.r. spectral data of (23) are given in our preliminary account of the photoaddition of enol ethers to 2-substituted anisoles.[28] ν_{max} (smear) 2240 cm^{-1}; M$^+$ calc. 205.1103, found m/z 205.1109. (24) δ(CDCl$_3$), 6.65 (1H,brd), 6.25 (1H,dd), 5.78 (1H,dd), 5.15 (1H,d), 3.50 (1H,dd), 3.45 (3H,s), 3.40 (2H,m), 2.40-2.10 (2H,m), and 1.05 (3H,t); λ_{max} (cyclohexane) 326 nm, ε 10,000 M^{-1}cm^{-1}. M$^+$ calc. 205.1103, found m/z 205.1103.

^{1}H N.m.r. spectra were recorded on a Perkin Elmer R-34 Spectrometer and structural assignments were confirmed by extensive decoupling experiments.

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References

1. See references in "Aromatic Photochemistry" in "Photochemistry", (Specialist Periodical Report), ed. D.Bryce-Smith, The Royal Society of Chemistry, London, Vols. 1-18.

2. D.Bryce-Smith and A.Gilbert, *Tetrahedron*, 1977, **33**, 2459.

3. J.Mattay, *J.Photochem.*, 1987, **37**, 167; J.Mattay, J.Runsink, R.Hertel, J.Kalbe and I.Schewe, *J.Photochem.*, 1987, **37**, 335.

4. D.Bryce-Smith, M.G.B.Drew, G.A.Fenton, and A.Gilbert, *J.Chem.Soc.Chem.Comm.*, 1985, 607.

5. J.Mattay, *Tetrahedron*, 1985, **41**, 2405.

6. D.Bryce-Smith, A.Gilbert and J.Mattay, *Tetrahedron*, 1986, **21**, 6011.

7. J.Mattay, J.Runsink, J.A.Piccirilli, A.W.H.Jans, and J.Cornelisse, *J.Chem.Soc.Perkin I*, 1987, 15; J.A.van der Hart, J.J.C.Mulder, and J.Cornelisse, *J.Molecular Structure*, 1987, **151**, 1.

8. M.Ohashi, T.Tanaka, and S.Yamada, *J.Chem.Soc.Chem.Comm.*, 1976, 800; N.Al-Jalal and A.Gilbert, *J.Chem.Research*, 1983, 266.

9. J.A.Ors and R.Srinivasan, *J.Org.Chem.*, 1977, **42**, 1321.

10. (a) A.Gilbert, G.N.Taylor, and A.Collins, *J.Chem.Soc.Perkin I*, 1980, 1218;
    (b) A.W.H.Jans, B.van Arkel, J.J. van Dijk-Knepper, H.Mioch and J.Cornelisse, *Tetrahedron*, 1984, **40**, 5071.

11. T.S.Cantrell, *J.Org.Chem.*, 1977, **42**, 4238.

12. M.G.B.Drew, A.Gilbert, P.Heath, A.J.Mitchell, and P.W.Rodwell, *J.Chem.Soc.Chem.Comm.*, 1983, 750; J.Cornelisse, A.Gilbert, and P.W.Rodwell, *Tetrahedron Letters*, 1986, *27*, 5003.

13. E.M.Osselton, E.L.M.Lempers and J.Cornelisse, *Rec.Trav.Chim.Pays-Bas*, 1985, *104*, 124.

14. N.Al-Jalal, M.G.B.Drew, and A.Gilbert, *J.Chem.Soc.Chem.Comm.*, 1985, 85.

15. Z.R.Grabowski, K.Rotkiewicz, A.Siemiarczuk, D.J.Cowley, and W.Baumann, *Nouv.J.Chim.*, 1979, *3*, 443.

16. Y.H.Lui and S.P.McGlynn, *J.Mol.Spectrosc.*, 1975, *55*, 163

17. F.Heisel and J.A.Miehe, *Chem.Phys.Lett.*, 1983, *100*, No. 2, 183, and references therein; R.J.Visser, C.A.G.O.Varma, J.Konijnenberg and P.C.M.Weisenborn, *J.Mol.Struct.*, 1984, *114*, 105.

18. E.M.Osselton, E.L.M.Lempers, C.P.Eyken, and J.Cornelisse, *Rec.Trav.Chim.Pays-Bas*, 1986, *105*, 171.

19. D.Bryce-Smith, B.E.Foulger, J.Forrester, A.Gilbert, B.H.Orger, and H.M.Tyrrell, *J.Chem.Soc.Perkin Trans.I*, 1980, 55.

20. R.S.Sheridan, *Tetrahedron Letters*, 1982, *23*, 267.

21. The photocycloaddition of *cis* cyclo-octene to benzonitrile occurs in a ratio of Φ *ortho* : Φ *meta* of 3:1 respectively, A.Gilbert and O.Griffiths unpublished observations.

22. D.Bryce-Smith, A.Gilbert, B.H.Orger, and H.M.Tyrrell, *Chem.Comm.*, 1974, 334.

23. A.Gilbert, G.N.Taylor, and M.W.bin Samsudin, *J.Chem.Soc.Perkin I*, 1980, 869.

24. A.Gilbert and P.Yianni, *Tetrahedron Letters*, 1982, *23*, 4611.

25. P.J.Wagner and K.Nahm, *J.Amer.Chem.Soc.*, 1987, *109*, 4404; K.B.Cosstick, M.G.B.Drew and A.Gilbert, paper accepted for publication in *J.Chem.Soc.Chem.Comm.*

26. The involvement of intermediates of type (21) in the *meta* photocycloaddition of ethenes to benzenoid compounds is fully discussed in references 3 to 7.

27. K.E.Wilzbach and L.Kaplan, *J.Amer.Chem.Soc.*, 1971, *93*, 2073.

28. A.Gilbert and P.Heath, paper accepted for publication in *Tetrahedron Letters*.