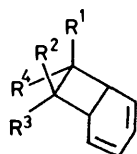# The Stereochemistry of 1,2-Photocycloaddition of Vinylic Compounds to Benzene †

By **Richard J. Atkins** and **Gordon I. Fray**,* School of Chemistry, The University, Bristol BS8 1TS

Andrew Gilbert,* **M. Wahid bin Samsudin**, **Andrew J. K. Steward**, and **Grahame N. Taylor**, Department of Chemistry, The University, Reading RG6 2AD

The stereochemistry of the 1,2-photocycloaddition of benzene to acrylonitrile, methyl acrylate, methyl methacrylate, methyl vinyl ketone, ethyl vinyl ether, butyl vinyl ether, 2,3-dihydropyran, and 2,3-dihydro-1,4-dioxin has been investigated. The evidence indicates that *exo*-1,2-adducts are formed exclusively from all these vinylic compounds except the acrylates and methyl vinyl ketone, which gave mixtures of *exo*- and *endo*-stereoisomers.
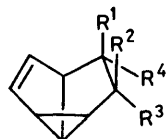
IRRADIATION of benzene at 254 nm in the presence of olefinic compounds can give rise to 1,2-, 1,3-, and less commonly 1,4-cycloadducts, having structures (1), (2), and (3) respectively. The relative quantum efficiencies of the 1,2- and 1,3-cycloaddition processes depend on the nature of the substituent groups attached to the ethylenic bond.[2,3] *Exclusive* 1,2-photocycloaddition to

(1)

(4) R^1, $R^2 = CO \cdot O \cdot CO$, $R^3 = R^4 = H$

(5) R^1, $R^2 = CO \cdot NH \cdot CO$, $R^3 = R^4 = H$

(8) $R^1 = CN$, $R^2 = R^3 = R^4 = H$

(16) $R^1 = CO_2Me$, $R^2 = R^3 = R^4 = H$

(17) $R^1 = R^2 = R^3 = H$, $R^4 = CO_2Me$

(22) $R^1 = CO_2Me$, $R^2 = R^3 = H$, $R^4 = Me$

(23) $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = CO_2Me$

(28) $R^1 = COMe$, $R^2 = R^3 = R^4 = H$

(29) $R^1 = R^2 = R^3 = H$, $R^4 = COMe$

(34) $R^1 = OEt$, $R^2 = R^3 = R^4 = H$

(40) R^1, $R^2 = -[CH_2]_3O-$

(42) $R^1 = R^2 = H$, $R^3 = R^4 = -[CH_2]_3O-$

(43) $R^1 = R^2 = -O[CH_2]_2O-$, $R^3 = R^4 = H$

(2)

(36) $R^1 = R^3 = R^4 = H$, $R^2 = OEt$

(37) $R^1 = R^2 = R^3 = H$, $R^4 = OEt$

(38) $R^1 = OEt$, $R^2 = R^3 = R^4 = H$

(3)

benzene is shown by maleic anhydride and maleimide, which moreover undergo the cycloaddition process in a stereospecific manner to form, initially, the *exo*-products
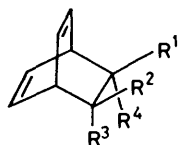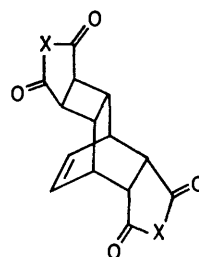

(6) X = O

(7) X = NH
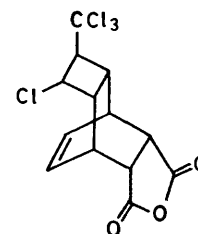
(9)

(4)[4,5] and (5)[6] respectively; subsequent *thermal* cycloaddition of these reactive dienophiles results in final products which are 1 : 2 adducts of benzene, (6) and (7), respectively. In other cases the dienophilic reactivity of the olefinic components may be insufficient for the production (at ambient temperature) of such 1 : 2 adducts, but treatment of the 1 : 1 photoadducts with *e.g.* maleic anhydride or (better) *N*-phenylmaleimide provides a ready and quantitative method for their separation from other photoproducts, and at the same time converts them into stable crystalline derivatives. The Diels–Alder addition of dienophiles such as maleic anhydride to bicyclo[4.2.0]octa-2,4-dienes invariably occurs on the unhindered face of the diene system, and in the *endo*-mode (see ref. 7).

In the present paper, the stereochemistry of the 1,2-photocycloaddition of several ethylenic compounds to benzene is defined and the results are discussed in the context of previous findings that the photoprocess is stereospecific, that ethylenes with electron-donor properties appear to undergo *endo*-cycloaddition whereas those with acceptor properties yield *exo*-products,[3] and that the preferred relative orientation of the addends in the ground-state may be an important factor in determining the stereochemistry of the 1,2-cycloadduct.[8]

RESULTS

We have examined the stereochemistry of the 1,2-photocycloaddition to benzene of acrylonitrile, methyl acrylate,

† For preliminary reports, see ref. 1.

methyl methacrylate, methyl vinyl ketone, ethyl vinyl ether, butyl vinyl ether, 2,3-dihydropyran, and 2,3-dihydro-1,4-dioxin. The 1 : 1 adducts of benzene with acrylonitrile, methyl acrylate, methyl vinyl ketone, and 2,3-dihydro-1,4-dioxin resulted exclusively from 1,2-cycloaddition, whereas with methyl methacrylate minor quantities of unidentified adducts were also formed, and the remaining vinylic ethers yielded various amounts of both 1,2- and 1,3-cycloadducts. The 1,2-photocycloaddition was found to be stereospecific for all the ethylenes examined except the acrylates and (contrary to our initial inference [1b]) methyl vinyl ketone.

The known [9] benzene–acrylonitrile photoadduct was shown to possess the *exo*-structure (8) as follows.[1a] Compound (9), of proved stereochemistry,[10] results from the free radical addition of carbon tetrachloride to the cyclo-octatetraene–maleic anhydride adduct, and may be converted into the chloro-tricarboxylic acid (10) by the action
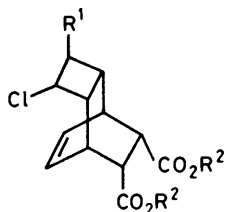
(10) R^1 = CO$_2$H, R^2 = H

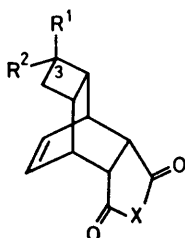(11) R^1 = CCl$_3$, R^2 = Me

(12) R^1 = CO$_2$Me, R^2 = Me
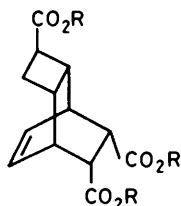
(13) R = Me

(14) R = H

(15) R^1 = CN, R^2 = H, X = O

(18) R^1 = CO$_2$Me, R^2 = H, X = NPh

(19) R^1 = H, R^2 = CO$_2$Me, X = NPh

(20) R^1 = CO$_2$H, R^2 = H, X = NPh

(24) R^1 = CO$_2$Me, R^2 = Me, X = NPh

(25) R^1 = Me, R^2 = CO$_2$Me, X = NPh

(26) R^1 = COMe, R^2 = H, X = NPh

(27) R^1 = H, R^2 = COMe, X = NPh

(32) R^1 = CN, R^2 = H, X = NPh

(33) R^1 = OEt, R^2 = H, X = NPh

(39) R^1 = OBu^n, R^2 = H, X = NPh

of concentrated sulphuric acid, followed by treatment with water.[10] The transformation of (9) into (10) involves no change of stereochemistry, as shown by comparison of the ^{1}H n.m.r. spectra of the derived esters (11) and (12).[1a] Dechlorination of the trimethyl ester (12) with tri-n-butyltin hydride gave a product (13) which was identical

with a sample obtained by esterification of the tricarboxylic acid (14), produced from the benzene–acrylonitrile photoadduct by addition of maleic anhydride and subsequent hydrolysis of the resulting nitrile-anhydride (15).[9] It may be noted here that the vinylic proton resonance in the n.m.r. spectrum of the Diels–Alder adduct (15) took the form of an apparent triplet (2 H); this already indicated an *exo*-configuration for the cyano-group [11,12] (an *endo*-substituent in the 3-position would be expected to perturb the resonance of one of the vinyl protons, giving rise to a more complex set of signals in the vinylic region [11]).

Unexpectedly, the major benzene–methyl acrylate photoproduct (isolated by preparative g.l.c.), which was accompanied by varying amounts (dependent upon the reactant concentrations) of cyclobutanes formed by photodimerisation of the unsaturated ester, was shown by its ^{1}H n.m.r. spectrum, and that of its Diels–Alder adduct with N-phenylmaleimide, to be a *ca.* 2 : 1 mixture of the *exo*- and *endo*-1,2-cycloadduct stereoisomers (16) and (17), respectively. Thus the n.m.r. spectrum of the main product was consistent with the general 1,2-cycloadduct structure but the signal due to the methoxycarbonyl protons was split, the two peak heights being in a ratio of *ca.* 2 : 1 with increasing field. Further, addition of portions of a europium shift reagent to the solution caused a more pronounced shift of the major ester proton resonance than of the minor, indicating a less hindered approach of the shift reagent in the former than in the latter case, and hence suggesting *exo*- and *endo*-geometries respectively. Reaction of the 1,2-photocycloadduct mixture with N-phenylmaleimide gave a mixture of two products as deduced from the n.m.r. spectrum, the significant features of which were the vinyl proton resonance, which consisted of an apparent triplet centred at δ *ca.* 6.5 and a multiplet at 6.3 in a ratio of *ca.* 2 : 1, and the methoxycarbonyl signal, which was again split in the ratio of 2 : 1 with increasing field. These results were interpreted in terms of a 2 : 1 mixture of the *exo-endo* and *endo-endo* adducts (18) and (19) respectively, authentic samples of which were then synthesised independently as follows. The *exo*-ester (18) was obtained from the carboxylic acid (20), produced from the tricarboxylic acid (14) by treatment of its cyclic anhydride with aniline. The route to the *endo*-ester (19) started from methoxycarbonyl-cyclo-octatetraene, prepared by the photoaddition of methyl propiolate to benzene.[13] The cyclo-octatetraene was converted into the maleic anhydride adduct (21),[14] hydrogenation of which (in the presence of Adam's catalyst) proceeded in a site-selective and stereoselective manner to afford, after reaction with aniline, the required *endo*-ester (19). The ^{1}H n.m.r. spectrum of a synthetic 2 : 1 mixture of the stereoisomers (18) and (19) was virtually identical with that of the original mixture prepared from the benzene–methyl acrylate 1,2-photocycloadduct by reaction with N-phenylmaleimide.

Irradiation of benzene solutions of methyl methacrylate yielded three 1 : 1 adducts, of which one constituted >85% of the mixture and furnished a second example of non-stereospecific 1,2-photocycloaddition to benzene. That this major 1 : 1 adduct was a 2 : 1 mixture of the *exo*- and *endo*-stereoisomers (22) and (23) was indicated by comparison of its ^{1}H n.m.r. spectrum with that of the methyl acrylate–benzene adduct mixture. This assignment was substantiated, as with the methyl acrylate product, by the ^{1}H n.m.r. spectrum of its Diels–Alder adduct with N-phenylmaleimide. As expected, the vinyl protons resonated as a

complex multiplet, and the two methyl resonances were split in the ratios 2 : 1 (CO_2CH_3) and 1 : 2 (CH_3) with increasing field. From this spectral evidence it could be deduced that the major isomer contains an *endo*-CH_3 group, which must lie in the shielding region of the ethylenic bond whereas the *exo*-CH_3 of the minor isomer should be comparatively unaffected by this structural moiety. The converse of course applies to the methoxycarbonyl groups in the two isomers, and structures (24) and (25) respectively

(21)

(30)

(31)

(35)

(41) X^1 = CH_2, X^2 = H

(44) X^1 = O, X^2 = Br
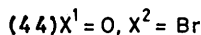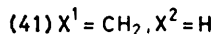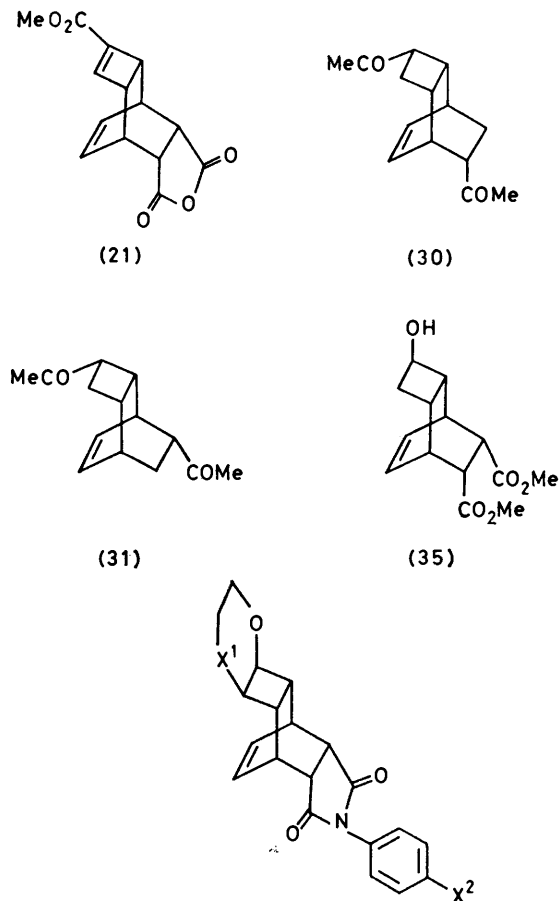
may therefore be assigned to the major and minor components of the Diels–Alder product. Thus for both methyl acrylate and methyl methacrylate the predominant 1,2-cycloadduct results from an initial photoaddition in the *exo*-mode with respect to the ester group. Since both *exo*- and *endo*-stereoisomers were formed, however, it was of interest to ascertain if the non-stereospecificity of the photoprocess was also followed by the related system methyl crotonate–benzene. Irradiation of the *E*-isomer in benzene produced essentially one product as judged by g.l.c. analysis, and although the ¹H n.m.r. spectrum indicated the basic 1,2-cycloadduct structure (2), both the methyl and the methoxycarbonyl proton resonances were split, again indicating the presence of stereoisomers. Unfortunately, under the experimental conditions methyl crotonate rapidly undergoes $E \longrightarrow Z$ isomerism. The absence of data on the

relative efficiencies of cycloaddition of the two geometrical isomers to benzene, coupled with the present inability to resolve the adduct mixture by chromatography, precludes meaningful structural assignments and the product may indeed be a mixture of all four possible isomers.

Initial experiments with methyl vinyl ketone indicated the formation of a single 1,2-photocycloadduct, showing an unsplit n.m.r. signal for the $COCH_3$ protons. The *N*-phenylmaleimide adduct, however, was clearly a *ca.* 1 : 1 mixture of the *exo-endo* and *endo-endo* structures (26) and (27) respectively from the appearance of the n.m.r. spectrum, in which the methyl signal was split and the vinyl protons gave rise to a ' triplet ' and a multiplet [*cf.* the mixture of (18) and (19)]. Moreover, examination of the initial photoadduct by means of g.c.–m.s. provided some confirmatory evidence for the presence of a mixture; thus multiple scanning by m.s. of the material eluted (as a single peak) from a g.c. column showed systematic changes in the ratios of the fragment ions, which did not vary with the sample size. We conclude that methyl vinyl ketone, like methyl acrylate, undergoes 1,2-photocycloaddition to benzene in a non-stereospecific manner, and that the product is a *ca.* 1 : 1 mixture of the stereoisomers (28) and (29). From one experiment, carried out at 42 °C instead of room temperature, there was isolated a 2 : 1 methyl vinyl ketone–benzene adduct, formulated with *endo-endo* stereochemistry, (30) and/or (31), on the basis of its ¹H n.m.r. spectrum (2 H multiplet signal in the vinyl proton region); the same reaction also yielded a 1 : 1 adduct which reacted with *N*-phenylmaleimide to give the *exo-endo* system (26) (the vinylic proton resonance appeared as a 2 H ' triplet ').

In view of the results obtained with methyl acrylate and methyl vinyl ketone, the acrylonitrile–benzene system was carefully re-examined, but in this case *exo*-1,2-photocycloaddition seems to be exclusive. Investigation of the photoadduct by g.c.–m.s., or ¹H n.m.r. spectroscopy in the presence of a shift reagent which separated the signal due to $>CH(CN)$, gave no indication of the presence of a mixture. The ¹H n.m.r. spectrum of the *N*-phenylmaleimide adduct unexpectedly showed two 1 H ' triplet ' signals in the vinylic region, but double irradiation experiments (in the presence of a shift reagent) revealed that the protons giving rise to these signals were spin–spin coupled and therefore contained in the same molecule. That the *N*-phenylmaleimide adduct possessed the *exo-endo* structure (32) was confirmed by its identity with the product obtained by treatment of the anhydride (15) with aniline.

Ethyl vinyl ether and benzene have previously been reported to yield a mixture of 1,2- and 1,3-cycloadducts, but no stereochemical assignments were made.[3] Only one 1,2-cycloadduct was formed in the present work, as evidenced by chromatographic and spectroscopic analysis of separated material. This adduct was conveniently isolated from the crude reaction mixture as its *N*-phenylmaleimide adduct, the spectroscopic and analytical data for which were consistent with its formulation as (33). *exo*-Stereochemistry for the ethoxy-group in (33), and hence in the initial adduct (34), was evident from the n.m.r. spectrum, in which the 2 H vinyl proton signal appeared as a ' triplet '; a more complex set of signals in the vinylic region is found for the corresponding Diels–Alder adduct of the 1,2-photocycloadduct from 1,1-dimethoxyethylene and benzene,[15] in accord with the presence of an *endo*-methoxy-group. This assignment was conclusively established by the unambiguous synthesis of (33), and comparison of the two

specimens. The synthesis involved hydroxymercuriation–demercuriation of the esterified cyclo-octatetraene–maleic anhydride adduct to give the hydroxy-diester (35),[12] followed by O-ethylation using ethyl iodide–silver oxide, hydrolysis of the ester groups with aqueous trifluoroacetic acid, thermal conversion of the resulting dicarboxylic acid to the cyclic anhydride, and finally reaction of this with aniline.

The residual oil remaining after removal of the exo-1,2-cycloadduct as its derivative (33) from the crude reaction mixture was found to comprise three further 1 : 1 adducts of ethyl vinyl ether and benzene, in the ratio 2.2 : 1.8 : 1 in order of increasing retention time on Carbowax 20M. These adducts were separated by preparative g.l.c. and shown to be the three 1,3-cycloadducts (36), (37), and (38) (order of decreasing abundance) by their spectroscopic properties and comparison with those of adducts of known structure.

Irradiation of n-butyl vinyl ether and benzene mixture gave broadly similar results to those described above for the ethyl vinyl ether system. In particular, the 1,2-cycloadduct was again shown to have exo-stereochemistry by the [1]H n.m.r. spectrum of its N-phenylmaleimide Diels–Alder adduct (39).

In contrast with the acyclic vinyl ethers, 2,3-dihydropyran and 2,3-dihydro-1,4-dioxin both showed high selectivity in their mode of photocycloaddition to benzene. Thus irradiation of 2,3-dihydropyran in benzene gave the 1,2-cycloadduct in a quantum yield ratio of >15 relative to other products, and the 1,2-mode of addition was essentially exclusive for the 2,3-dihydro-1,4-dioxin–benzene system. The former photoadduct could be formulated as the exo-compound (40) from the [1]H n.m.r. spectrum of its N-phenyl-maleimide derivative (41). The endo-structure (42) originally assigned [16] was based on the differing chemical shifts shown by the geminal protons in the methylene groups in positions α and β relative to the oxygen atom in the 1 : 1 photoadduct; the non-equivalence of these protons is now considered to be a result of the conformation of the heterocyclic ring rather than a shielding effect of the diene π-system.

The general appearance of the vinyl proton signals in the Diels–Alder adducts cannot, of course, help in determining the stereochemistry of 1,2-photocycloadducts derived from Z-1,2-symmetrically substituted ethylenes such as 2,3-dihydro-1,4-dioxin. In this case the exo-stereochemistry of the product (43) was proved by X-ray crystallographic analysis of the N-p-bromophenylmaleimide adduct (44), the details of which have been published elsewhere.[1c]

DISCUSSION

It has been demonstrated that the dienophilic ethylenes maleic anhydride and maleimide form ground-state complexes with benzene which exhibit charge-transfer absorption,[17] and it has been deduced from n.m.r. spectroscopic solvent-shift studies that in these complexes the components are oriented in the exo-fashion.[18] Subsequent investigations [8] have revealed that a wide variety of ethylenic compounds form weak ' dark ' complexes with benzene, and it has been proposed that the preferred orientation of the molecules is determined by the electron-donating or -accepting character of the ethylene relative to benzene, as determined by ionisation potential. Thus ethylenes having

ionisation potentials lower than that of benzene (9.24 eV) (i.e. electron-donor ethylenes) appear to adopt endo-orientations relative to benzene, whereas exo-stereochemistry is preferred by electron-deficient ethylenes.

In previous work the stereochemistry of the benzene 1,2-cycloadducts from (Z)-but-2-ene,[19] (Z)-cyclo-octene,[20] maleic anhydride,[4,5] and maleimide [6] has been elucidated, and it has been noted that the endo-geometry found in the first two cases and the exo-geometry of the last two specifically reflects the preferred orientation in the ground state.[3] The stereochemical assignment for the 1,2-cycloadduct of benzene with the electron-acceptor acrylonitrile is consistent with the proposal that the orientation of the addends in the weak ground-state complexes is important in determining the stereochemistry of the addition reaction; the results obtained with the vinyl ethers, however, are not in accord with this suggestion. Thus although the loose ground-state complexes of benzene with both acyclic and cyclic vinyl ethers appear to prefer an endo-arrangement of the components, the stereochemistry of the 1,2-photocycloadducts is specifically exo in all cases. This result is all the more surprising in view of the recent observation that the exo-stereochemistry found [21] for the 1,2-cycloadduct of 2,2-dimethyl-1,3-dioxole and benzene parallels the preferred orientation of the addends in the ground-state as inferred from n.m.r. spectroscopy.* The reason for the change in stereochemistry, in the particular case of vinyl ethers, in going from a weak ground-state complex through an excited-state to the 1,2-cycloadduct is not obvious, but this feature may well reflect a difference in preferred orientation between a ground- and an excited-state complex, the intermediacy of which in alkene–arene photocycloadditions has previously been postulated and discussed.[19,22,23] A preferred orientation of the addends in an exciplex has been proposed to explain the exclusive endo-2,6-cycloaddition of a number of alkenes to toluene and anisole,[24] but other workers have reported exceptions to this specificity.[25]

In general 1,3-cycloaddition of ethylenes to benzene yields a mixture of exo- and endo-isomers, in which the latter frequently predominates and is on occasion the exclusive product.[2,24] Non-stereospecific 1,2-cycloaddition has been observed in the present work with acrylic esters, which yielded mixtures of stereoisomers in which those with the electron-withdrawing group exo to the cyclohexa-1,3-diene moiety were formed in the greater yield, as might have been expected from the results with maleic anhydride, maleimide, and acrylonitrile. Methyl vinyl ketone behaved similarly, except that the exo- and endo-stereoisomers were formed in almost equal amounts. This lack of stereospecificity may result from non-concerted cycloaddition and the involvement of triplet rather than, or as well as, singlet intermediates, as is observed in the photoaddition of dimethyl

fumarate to phenanthrene;[26] alternatively, it may reflect a non-specific orientation of the addends in the ground-state and/or in a possible exciplex of the reactants. The latter alternative is more open to speculation than proof. Weak ground-state complexes between benzene and steroidal carbonyl compounds have previously been observed by [1]H n.m.r. spectroscopy.[27] In these cases the dominant factor is the interaction of the ring π-electrons with the partial positive charge on the carbonyl carbon atom, such that the π-electrons are as far as possible from the partial negative charge on the oxygen. For the acrylates and methyl vinyl ketone, however, the n.m.r. spectroscopic solvent-induced shifts are difficult to interpret in terms of preferred *exo*- or *endo*-arrangements of the addends. Thus *all* the proton resonances in methyl acrylate and in methyl vinyl ketone are shifted to higher field in benzene, and of those in methyl methacrylate, only the lowest-field vinylic proton suffers a downfield shift.

Preliminary attempts to implicate triplet intermediates as the source of the non-specific reactions have not been conclusive, but with methyl acrylate and methyl vinyl ketone the ratio of the 1,2-cycloadducts to the ethylene dimers increased with the concentration of benzene, which is the reverse of the situation found with norbornene,[28] cyclohexene,[29] and cyclohexa-1,4-diene.[30] Since the yield of T_1 benzene increases with benzene concentration,[31] the present preliminary results may indicate that the 1,2-photocycloaddition of acrylates and methyl vinyl ketone to benzene is a triplet process and that T_1 benzene does not sensitise the ethylene dimer formation.

To summarise, we have determined the stereochemistry of several 1,2-photocycloadducts of vinylic compounds and benzene with the general objective of investigating the stereospecificity of this photoprocess. A further example of an electron-deficient ethylene, acrylonitrile, has been found to yield a specifically *exo*-adduct. In the case of vinyl ethers, at least, the preferred orientation of the addends in their weak ground-state complexes is unimportant in determining the stereochemistry of the 1,2-cycloaddition to benzene, since these also gave exclusively *exo*-products. Contrasting with these and all previously reported 1,2-photocycloadditions, non-stereospecific cycloaddition occurred with acrylic esters and methyl vinyl ketone.

EXPERIMENTAL

Unless stated otherwise, [1]H n.m.r. spectra were measured at 100 MHz using CDCl_3 solutions, i.r. spectra were determined for liquid films, and cyclohexane was used as the solvent for u.v. spectral measurements.

Preparation of the Benzene–Olefin 1,2-Photocycloadducts.—An equivolume mixture of the olefinic compound and benzene, contained in a quartz tube under air at 20 °C, was irradiated with a Hanovia low-pressure mercury arc (rated 15 W). The only exception to this general procedure was with 2,3-dihydro-1,4-dioxin; in this case the 10% ethereal solution obtained by the published preparative method[32] was mixed with an equal volume of benzene. Adduct for-

mation was monitored by g.l.c. using Carbowax 20M as the liquid phase, except for the alkyl vinyl ether adducts when Apiezon L was employed; the liquid phase used in following the $E \rightarrow Z$ photoisomerisation of methyl crotonate was dinonyl phthalate.

The starting materials were removed from the irradiated solution at water-pump pressure using a rotary evaporator, and where appropriate were recycled. The photoadduct was then distilled from the oily yellow-orange residue under oil-pump vacuum. The resulting 1,2-cycloadducts from methyl crotonate, 2,3-dihydropyran, and 2,3-dihydro-1,4-dioxin were sufficiently pure for spectroscopic identification; in other cases separation from impurities was achieved either by further (fractional) distillation, or by preparative g.l.c. using the liquid phases specified above. The impurities encountered in various amounts in the different systems included 2 : 1 olefin–benzene adducts (acrylonitrile and methyl vinyl ketone), ethylene dimers (methyl acrylate), and other 1 : 1 benzene adducts (methyl methacrylate and the alkyl vinyl ethers). All the 1,2-cycloadducts gave mass spectra (parent ions and fragmentations) wholly consistent with their structural assignments.

Reactions of the 1,2-Cycloadducts with Dienophiles.—The 1,2-cycloadducts, either purified as described above or in admixture with other photoproducts after simple distillation, reacted quantitatively (as judged by g.l.c.) with maleic anhydride or N-phenylmaleimide. The general reaction conditions involved heating a ca. 10% w/v solution of the 1,2-cycloadduct in refluxing diethyl ether with excess of the dienophile for 6 h, and then allowing the mixture to stand overnight at 8 °C. The resulting 1 : 1 : 1 adducts (molecular weights confirmed by mass spectra) were filtered off and recrystallised from ethanol (unless stated otherwise).

Data permitting the identification of the 1,2-cycloadducts are recorded below.

7-exo-*Cyanobicyclo*[4.2.0]*octa-2,4-diene* (8) had δ (60 MHz) 6.0—5.3 (4 H), 3.6—3.0 (3 H), and 3.0—1.7 (2 H) (for i.r. and u.v. spectra, see ref. 9). Maleic anhydride adduct (15) had m.p. 249—250 °C (lit.,[9] 248—248.5 °C) (from acetone); δ (60 MHz; CF_3CO_2H) 6.9—6.4 (2 H, apparent t), 3.7—3.4 (2 H), 3.4—3.1 (2 H), 3.1—2.7 (2 H), 2.7—2.3 (2 H), and 2.3—1.9 (2 H) (for i.r. spectrum, see ref. 9). N-Phenyl-maleimide *adduct* (32) had m.p. 245—248 °C (Found: C, 74.7; H, 5.55; N, 9.0. $C_{19}H_{16}N_2O_2$ requires C, 75.0; H, 5.3; N, 9.2%); $\nu_{max.}$ (Nujol) 1 775 and 1 705 cm⁻¹; δ 7.6—7.1 (5 H), 6.85—6.6 (1 H, apparent t), 6.55—6.3 (1 H, apparent t), 3.6—3.1 (4 H), 3.0—2.35 (3 H), and 2.2—1.8 (2 H).

7-Methoxycarbonylbicyclo[4.2.0]octa-2,4-diene [mixture of stereoisomers (16) and (17)] had $\nu_{max.}$ 1 740 cm⁻¹; $\lambda_{max.}$ 280 nm (ε 2 950); δ (60 MHz) 6.0—5.2 (4 H), 3.65 (3 H, split s), and 3.4—2.1 (5 H). N-Phenylmaleimide adduct [mixture of (18) and (19)] had m.p. 188—190 °C; δ 7.55—7.1 (5 H), 6.55—6.1 (2 H, apparent t together with m), 3.7 (3 H, split s), 3.65—3.2 (2 H), 2.95—2.8 (2 H), and 2.8—1.6 (5 H).

7-Methoxycarbonyl-7-methylbicyclo[4.2.0]octa-2,4-diene [mixture of stereoisomers (22) and (23)] had $\nu_{max.}$ 1 740 cm⁻¹; $\lambda_{max.}$ 278 nm (ε 2 960); δ (60 MHz, CCl_4) 6.0—5.2 (4 H), 3.67 (3 H, ill-defined split s), 3.5—1.7 (4 H), and 1.4 (3 H, split s). N-Phenylmaleimide adduct [mixture of (24) and (25)] had m.p. 196—198 °C; δ (60 MHz) 7.6—7.0 (5 H), 6.5—6.1 (2 H), 3.7 (3 H, split s), 3.6—3.1 (2 H), 3.0—2.7 (2 H), 2.6—1.65 (4 H), and 1.45—1.2 (3 H, split s).

7-Methoxycarbonyl-8-methylbicyclo[4.2.0]octa-2,4-diene

(mixture of stereoisomers) had $v_{max.}$ 1 740 cm^{-1}; $\lambda_{max.}$ 278 nm (ε 3 050); δ (60 MHz; CCl$_4$) 6.0—5.3 (4 H), 3.6 (3 H, split s), 3.4—2.4 (4 H), and 1.4—1.0 (3 H, split s).

7-Acetylbicyclo[4.2.0]octa-2,4-diene [mixture of stereoisomers (28) and (29)] had $v_{max.}$ 1 710 cm^{-1}; $\lambda_{max.}$ 275 nm (ε 2 800); δ (60 MHz) 6.0—5.5 (4 H), 4.4—1.9 (2 H), and 2.0 (3 H, s). N-Phenylmaleimide adduct [mixture of (26) and (27)] had m.p. 160—165 °C; δ 7.5—7.1 (5 H), 6.55—6.4 (ca. 1 H, apparent t), 6.35—6.15 (ca. 1 H, m), and 3.7—1.6 (9 H, together with a well defined 3 H split s at 2.1).

On one occasion when the irradiation was carried out at 42 °C, distillation of the crude product gave two fractions. The first, b.p. 80—110 °C at 0.05 mmHg, was essentially the 1 : 1 photoadduct (28). N-Phenylmaleimide adduct had m.p. 174—176 °C; $v_{max.}$ 1 770 and 1 705 cm^{-1}; δ 7.5—7.1 (5 H), 6.55—6.4 (2 H, apparent t), 3.45—3.15 (2 H), and 2.95—1.6 (7 H, together with an unsplit 3 H s at 2.1).

The second distillation fraction, b.p. 120—140 °C at 0.05 mmHg, partially crystallised on storage at −10 °C. Treatment with pentane–ether (2 : 1) then afforded the 2 : 1 adduct (30) and/or (31), m.p. 100—102 °C (Found: M, 218.1306. C$_{14}$H$_{18}$O$_2$ requires M, 218.1338); $v_{max.}$ 1 700 cm^{-1}; δ 6.55—6.15 (2 H, m) and 3.05—1.35 (10 H, with two superimposed 3 H s resonances at 2.15 and 2.04).

7-exo-Ethoxybicyclo[4.2.0]octa-2,4-diene (34) had $\lambda_{max.}$ (n-hexane) 274 nm (ε 3 100); δ 5.9—5.3 (4 H), 3.30 (2 H, q, J 7 Hz), 3.05—2.7 (1 H), 2.6—2.2 (2 H), 1.95—1.65 (1 H), and 1.1 (3 H, t, J 7 Hz). N-Phenylmaleimide adduct (33) had m.p. 166—167 °C (Found: C, 74.0; H, 6.8; N, 4.2. C$_{20}$H$_{21}$NO$_3$ requires C, 74.3; H, 6.55; N, 4.3%); $v_{max.}$ (Nujol) 1 775 and 1 700 cm^{-1}; δ 7.5—7.05 (5 H), 6.45—6.25 (2 H, apparent t), 3.6—3.15 (5 H), 2.9—2.85 (2 H), 2.65—2.45 (2 H), 2.15—1.7 (2 H), and 1.18 (3 H, t, J 7 Hz).

7-exo-n-Butoxybicyclo[4.2.0]octa-2,4-diene. N-Phenylmaleimide adduct (39) had m.p. 128.5—130 °C (from hexane) (Found: C, 75.3; H, 7.5; N, 3.8. C$_{22}$H$_{25}$NO$_3$ requires C, 75.2; H, 7.2; N, 4.0%); $v_{max.}$ (Nujol) 1 775 and 1 710 cm^{-1}; δ 7.55—7.05 (5 H), 6.5—6.3 (2 H, apparent t), 3.6—3.1 (5 H), 2.85 (2 H, d, J 3 Hz), 2.7—2.5 (2 H), 2.1—1.7 (2 H), 1.7—1.1 (4 H), and 0.9 (3 H, t, J 7 Hz).

anti-9-Oxatricyclo[6.4.0.0^{2,7}]dodeca-3,5-diene (40) had $\lambda_{max.}$ 275 nm (ε 2 960); δ (220 MHz; C$_6$D$_6$) 5.85—5.5 (4 H), 4.45—4.25 (1 H), 3.75—3.5 (1 H), 3.3—3.1 (1 H), 3.1—2.9 (1 H), 2.9—2.7 (1 H), 2.7—2.5 (1 H), 1.6—1.3 (3 H), and 1.3—1.0 (1 H). N-Phenylmaleimide adduct (41) had m.p. 178—180 °C (Found: C, 74.9; H, 6.5; N, 4.2. C$_{21}$H$_{21}$NO$_3$ requires C, 75.2; H, 6.3; N, 4.2%); $v_{max.}$ (Nujol) 1 775 and 1 710 cm^{-1}; δ (60 MHz) 7.5—7.1 (5 H), 6.4—6.2 (2 H, apparent t), 3.6—3.15 (4 H), 2.85—2.75 (2 H), 2.6—2.3 (2 H), and 2.0—1.3 (6 H).

anti-9,12-Dioxatricyclo[6.4.0.0^{2,7}]dodeca-3,5-diene (43) had $\lambda_{max.}$ 275 nm (ε 3 400); δ (60 MHz; C$_6$D$_6$) 5.8—5.6 (4 H), 4.4—4.3 (2 H), 3.5—3.3 (4 H), and 3.25—3.15 (2 H). N-p-Bromophenylmaleimide adduct (44) had m.p. 275—276 °C (Found: C, 58.05; H, 4.6; Br, 19.0; N, 3.2. C$_{20}$H$_{18}$BrNO$_4$ requires C, 57.7; H, 4.4; Br, 19.2; N, 3.4%); $v_{max.}$ 1 770 and 1 710 cm^{-1}; δ[(CD$_3$)$_2$CO] 7.75—7.55 (2 H, d, J 8 Hz), 7.1—6.9 (2 H, d, J 8 Hz), 6.65—6.45 (2 H, apparent t), 4.3—3.7 (6 H), 3.7—3.5 (2 H), 3.35—3.2 (2 H), and 3.15—3.0 (2 H).

The Chloro-trimethyl Ester (12).—The chloro-tricarboxylic acid (10)[10] was converted into the trimethyl ester (12) using methanolic sulphuric acid in the usual way, m.p. 104—106 °C (from methanol) (Found: C, 55.8; H, 5.65; Cl, 10.7. C$_{16}$H$_{19}$ClO$_6$ requires C, 56.1; H, 5.6; Cl, 10.3%); $v_{max.}$

(Nujol) 1 737 and 1 725 cm^{-1}; δ 6.7—6.3 (2 H), 4.85—4.6 (1 H), 3.70 (3 H, s), 3.63 (6 H, s), and 3.25—2.55 (7 H).

The Trimethyl Ester (13).—(a) A mixture of the chlorotrimethyl ester (12) (0.90 g), tri-n-butyltin hydride[33] (3 ml), azobisisobutyronitrile (10 mg), and dry toluene (40 ml) was heated under reflux in an atmosphere of nitrogen overnight. Removal of the solvent followed by crystallisation of the oily residue from light petroleum (b.p. 60—80 °C) gave the trimethyl ester (13) (0.50 g) (70%), m.p. 86—87 °C (Found: C, 62.1; H, 6.45. C$_{16}$H$_{20}$O$_6$ requires C, 62.3; H, 6.5%); $v_{max.}$ (Nujol) 1 745sh and 1 730 cm^{-1}; δ 6.6—6.4 (2 H, apparent t), 3.66 (3 H, s), 3.60 (6 H, s), 3.15—2.05 (8 H), and 1.85—1.55 (1 H).

(b) Esterification (methanolic sulphuric acid) of the tricarboxylic acid (14), prepared from the benzene–acrylonitrile photoadduct as described by Job and Littlehailes,[9] gave a product identical with the previous specimen.

The N-Phenylimido-exo-carboxylic Acid (20).—The tricarboxylic acid (14) (0.24 g) was kept at 150—160 °C (bath) and 0.1 mmHg for 2 h, and the resulting cyclic anhydride ($v_{max.}$ 1 848, 1 780, and 1 706 cm^{-1}) was then heated with aniline under reflux for 7 min. Addition of dilute hydrochloric acid afforded a crystalline precipitate, which was filtered off, washed with water, and dried to give the N-phenylimido-carboxylic acid (20) (0.25 g, 86%), m.p. 259—260 °C (decomp.) (from acetone) (Found: C, 70.5; H, 5.5; N, 4.1. C$_{19}$H$_{17}$NO$_4$ requires C, 70.6; H, 5.3; N, 4.3%); $v_{max.}$ (Nujol) 1 772, 1 707, and 1 688 cm^{-1}; δ[(CD$_3$)$_2$SO] 8.04br (1 H, s), 7.55—6.8 (5 H), 6.45—6.15 (2 H, apparent t), 3.4—2.0 (8 H), and 1.8—1.4 (1 H).

Esterification with diazomethane in ether–methanol gave the methyl ester (18), m.p. 204—205 °C (from acetone–ether) (Found: C, 70.7; H, 5.8; N, 4.1. C$_{20}$H$_{19}$NO$_4$ requires C, 71.2; H, 5.7; N, 4.15%); $v_{max.}$ (Nujol) 1 775, 1 729, and 1 707 cm^{-1}; δ 7.35—7.10 (5 H), 6.5—6.4 (2 H, apparent t), 3.70 (3 H, s), 3.5—3.2 (2 H), and 3.05—1.6 (7 H).

The N-Phenylimido-endo-methyl Ester (19).—The methoxycarbonylcyclo-octatetraene–maleic anhydride adduct (21)[14] (0.21 g), in glacial acetic acid (15 ml) was hydrogenated in the presence of pre-reduced Adam's catalyst at room temperature and atmospheric pressure. After 30 min ca. 1 equiv. of hydrogen had been absorbed, and the catalyst was removed by filtration. Evaporation of the filtrate gave an oily residue ($v_{max.}$ 1 860, 1 838, 1 777, and 1 727 cm^{-1}), which was heated under reflux with aniline (3 ml) for 5 min. The solution was acidified with dilute hydrochloric acid, and the product was collected by filtration, washed with water, and dried to afford the N-phenylimido-endo-methyl ester (19) (0.23 g, 84.5%), m.p. 187—188 °C (from acetone) (Found: C, 71.4; H, 5.8; N, 4.3. C$_{20}$H$_{19}$NO$_4$ requires C, 71.2; H, 5.7; N, 4.15%); $v_{max.}$ (Nujol) 1 775, 1 734, and 1 708 cm^{-1}; δ 7.55—7.05 (5 H), 6.45—6.05 (2 H), 3.68 (3 H, s), and 3.7—2.00 (9 H).

The exo-Ethoxy-N-phenylimide (33).—Crude exo-hydroxy-dimethyl ester (35) (0.51 g), obtained essentially as described by Mehta and Pandey,[12] was dissolved in ethyl iodide (3 ml) and the solution was stirred under reflux with freshly prepared, activated silver oxide (0.6 g) for 20 h. Filtration, followed by removal of ethyl iodide from the filtrate, afforded the exo-ethoxy-dimethyl ester, which was hydrolysed by heating in refluxing 20% aqueous trifluoroacetic acid (5 ml) for 1.5 h. Evaporation of the solution under reduced pressure yielded the exo-ethoxy-dicarboxylic acid, which was kept at 160 °C (bath) and 0.5 mmHg for 5 h.

The resulting cyclic anhydride [$\nu_{max.}$ (Nujol) 1 855 and 1 780 cm^{-1}] was then heated in refluxing aniline (2 ml) for 10 min. Addition of dilute hydrochloric acid gave a crystalline precipitate, which was collected, washed with water, dried, and finally recrystallised from acetone–ether to afford the *exo*-ethoxy-*N*-phenylimide (33) (0.20 g), identical with the previously described specimen.

REFERENCES

[1] (*a*) R. J. Atkins, G. I. Fray, and A. Gilbert, *Tetrahedron Letters*, 1975, 3087; (*b*) R. J. Atkins, G. I. Fray, A. Gilbert, and M. W. bin Samsudin, *ibid.*, 1977, 3597; (*c*) R. J. Atkins, G. I. Fray, M. G. B. Drew, A. Gilbert, and G. N. Taylor, *ibid.*, 1978, 2945.
[2] D. Bryce-Smith and A. Gilbert, *Tetrahedron*, 1976, **32**, 1309; 1977, **33**, 2459.
[3] D. Bryce-Smith, A. Gilbert, B. H. Orger, and H. M. Tyrrell, *J.C.S. Chem. Comm.*, 1974, 334.
[4] D. Bryce-Smith, B. Vickery, and G. I. Fray, *J. Chem. Soc.* (*C*), 1967, 390.
[5] W. Hartmann, H. G. Heine, and L. Schrader, *Tetrahedron Letters*, 1974, 883, 3101.
[6] D. Bryce-Smith and M. A. Hems, *Tetrahedron Letters*, 1966, 1895.
[7] G. I. Fray and R. G. Saxton, ' The Chemistry of Cyclo-octatetraene and Its Derivatives,' Cambridge University Press, Cambridge, 1978, pp. 219—220 and 248—250.
[8] D. Bryce-Smith, A. Gilbert, and H. M. Tyrrell, *J.C.S. Chem. Comm.*, 1974, 699.
[9] B. E. Job and H. D. Littlehailes, *J. Chem. Soc.* (*C*), 1968, 886.
[10] G. I. Fray, G. R. Geen, D. I. Davies, L. T. Parfitt, and M. J. Parrott, *J.C.S. Perkin I*, 1974, 729.

[11] J. P. Snyder and D. G. Farnum, *J. Org. Chem.*, 1966, **31**, 1699.
[12] G. Mehta and P. N. Pandey, *J. Org. Chem.*, 1975, **40**, 3631.
[13] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 1963, 695; G. L. Grunewald, J. M. Grindel, P. N. Patil, and K. N. Salman, *J. Medicin. Chem.*, 1976, **19**, 10.
[14] L. A. Paquette, R. S. Beckley, and W. B. Farnham, *J. Amer. Chem. Soc.*, 1975, **97**, 1089.
[15] A. Gilbert and M. W. bin Samsudin, unpublished work.
[16] A. Gilbert and G. N. Taylor, *Tetrahedron Letters*, 1977, 469.
[17] D. Bryce-Smith, B. E. Connett, and A. Gilbert, *J. Chem. Soc.* (*B*), 1968, 816; M. A. Hems, Ph.D. Thesis, Reading University, 1967.
[18] D. Bryce-Smith and M. A. Hems, *J. Chem. Soc.* (*B*), 1968, 812.
[19] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073.
[20] H. M. Tyrrell and A. P. Wolters, *Tetrahedron Letters*, 1974, 4193.
[21] H.-D. Scharf and J. Mattay, *Tetrahedron Letters*, 1977, 401; J. Mattay, H. Leismann, and H.-D. Scharf, *Chem. Ber.*, 1979, **112**, 577.
[22] W. I. Feree, J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **93**, 5502; R. C. Dougherty, *ibid.*, p. 7187.
[23] H. Leismann and J. Mattay, *Tetrahedron Letters*, 1978, 4265.
[24] R. Srinivasan, *J. Amer. Chem. Soc.*, 1971, **93**, 3555; J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *ibid.*, 1973, **95**, 6197; J. A. Ors and R. Srinivasan, *J. Org. Chem.*, 1977, **42**, 1321.
[25] D. Bryce-Smith, W. M. Dadson, A. Gilbert, B. H. Orger, and H. M. Tyrell, *Tetrahedron Letters*, 1978, 1093.
[26] D. Creed and R. A. Caldwell, *J. Amer. Chem. Soc.*, 1974, **96**, 7369; R. A. Caldwell and L. Smith, *ibid.*, p. 2994; S. Farid, S. E. Hartman, J. C. Doty, and J. L. R. Williams, *ibid.*, 1975, **97**, 3697; R. A. Caldwell and D. Creed, *ibid.*, 1977, **99**, 8360.
[27] N. S. Bhacca and D. H. Williams, *Tetrahedron Letters*, 1964, 3127.
[28] R. Srinivasan, *J. Phys. Chem.*, 1972, **76**, 15.
[29] H. M. Tyrrell, Ph.D. Thesis, Reading University, 1974.
[30] J. Forrester, Ph.D. Thesis, Reading University, 1977.
[31] R. B. Cundall and D. A. Robinson, *J.C.S. Faraday II*, 1972, 1691.
[32] L. M. Fieser and M. Fieser, ' Reagents for Organic Synthesis,' Wiley, New York, 1967, vol. I, p. 630.
[33] G. J. M. van der Kerk, J. G. Noltes, and J. G. A. Luijten, *J. Appl. Chem.*, 1957, **7**, 366