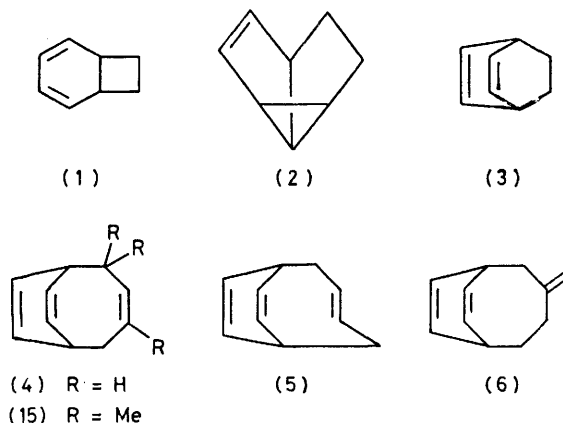


The Photochemical Reactions of Benzene with 1,2-, 1,3-, and 1,4-Dienes

By John C. Berridge, John Forrester, Brian E. Foulger, and Andrew Gilbert,* Department of Chemistry, University of Reading, Whiteknights, Reading, Berkshire RG6 2AD

The photocycloaddition reactions of benzene with 1,2-, 1,3-, and 1,4-dienes are described. Propa-1,2-diene (allene) and cyclonona-1,2-diene are unique among hydrocarbon ethylenic systems since 1,2-*para*-cycloaddition to the benzene ring is the major mode of reaction. The *meta*-cycloaddition of 1,2-dienes is regiospecific and this is accounted for by a mechanism involving prior *meta*-bonding in the arene leading to a polarised prefulvene species which undergoes 1,2-addition to the diene. The conformationally fixed *cis*-diene 1,2-dimethylenecyclohexane undergoes selective 1,4-*para*- and 1,4-*meta*-photocycloaddition to benzene whereas the reaction with 3-methylenecyclohexene is of low yield and non-selective giving diene dimers, substitution products, and adducts. Penta-1,4-diene and cyclohexa-1,4-diene yield 1,2-*meta*-cyclo-adducts with benzene, and evidence is presented for formation of 1,2-*para*-cycloadducts from each system: diene dimers are also produced in the latter case but solutions of bicyclo[2.2.1]hepta-2,5-diene in benzene are essentially inert photochemically.

SINCE the early reports that benzene and its simple derivatives form *ortho*- (1), *meta*- (2), and, less commonly, *para*-photocycloadducts (3) with ethylenes¹⁻⁵ and *cis*- and *trans*-*para*-1,4-photocycloadducts (4) and (5) with



1,3-dienes,⁶ numerous examples of photochemical addition reactions of arenes with ethylenic systems have been described.^{7,8} Factors which affect the relative efficiencies of the *ortho*- and *meta*-cycloaddition processes have been discussed^{7,9-14} but in all reported examples, the *para*-addition of simple ethylenes to photoexcited benzene is a minor reaction⁵ and has received comparatively little attention.† It has been proposed that all three processes arise from the S_1 state of benzene^{5,16} and that exciplexes are the adduct precursors.^{5,16,17} Such intermediates are also considered to be involved in the 1,3-diene-arene reactions¹⁸ which, in general, lead to complex mixtures of 1:1 adducts and diene dimers. There is, however, experimental evidence to show that the ground-state conformation of a 1,3-diene can determine its mode of photoreaction with benzene,¹⁹ and additions in the presence of iodine give synthetically useful amounts of (4) and (6) from benzene with buta-1,3-diene²⁰ and isoprene²¹ respectively.

In contrast to the photoprocesses of ethylenes and

† For reports of the *para*-photocycloaddition of triplet dichlorovinylene carbonate to benzene see ref. 15.

1,3-dienes, the reactions of acyclic and cyclic 1,2- and 1,4-dienes with photoexcited benzene have been totally neglected. In the present paper we describe and discuss the photoreactions of benzene with allene (propa-1,2-diene),²² cyclonona-1,2-diene,²² penta-1,4-diene, cyclohexa-1,4-diene, and bicyclo[2.2.1]hepta-2,5-diene and compare these with those of hydrocarbon monoenes. For comparison also with these systems we have investigated the reactions of benzene with certain 1,3-dienes but unlike previous studies with this arene ours have involved conformationally fixed dienes since these avoid the problems of addend isomerisation and subsequent side reactions which beset conformationally flexible systems.²³

RESULTS AND DISCUSSION

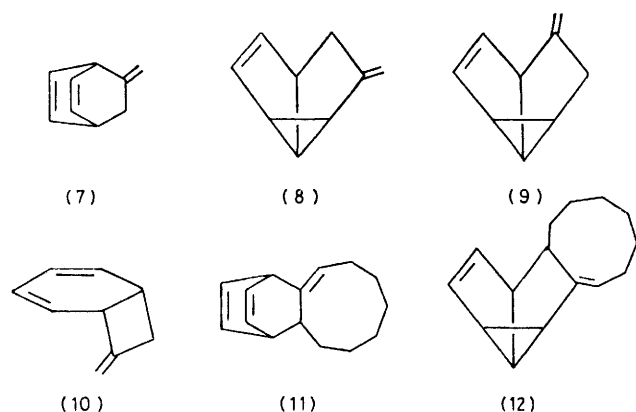
In all experiments the radiation source comprised low-pressure mercury-arc lamps. Nitrogen degassing generally had no significant effect on reaction efficiencies or product ratios within the time limits of the experiments and preparative irradiations were conducted under air.

Mixtures of products were formed in all cases and, with the exception of those from the conformationally fixed diene and benzene, the components were isolated by preparative g.l.c. Adduct structures were assigned essentially from spectroscopic data and their comparison with those of compounds of known structures: spectroscopic features which allow the assignment of *meta*-cycloadduct structures (*i.e.* the presence of the ethenylcyclopropane moiety) to products are well-documented^{2,5,10,24} and such aspects are not further argued here in detail.

(a) *Irradiation of Benzene with 1,2-Dienes.*—In 1,2-dienes, the π -systems of the two ethylenic units lie perpendicular to one another and thus they generally react as simple monoalkenes in their thermal²⁵ and photochemical cycloadditions.²⁶ It was to be expected, therefore, from previous studies with acyclic and cyclic alkenes, that with S_1 benzene, 1,2-dienes would yield *meta*-cycloadducts as the major reaction products.¹⁰ The 254 nm irradiation of benzene-1,2-diene mixtures

has been previously investigated but only the photo-sensitised reaction of the 1,2-diene was described and products derived from intermolecular addition were not reported.²⁷

In the present study we observed that irradiation of allene as a 5% v/v solution in benzene gave very low yields of four 1 : 1 adducts [$M^+ = 118$ m.u. (m.s.-g.l.c.)] in an approximate ratio of 2 : 12 : 6 : 1 (elution sequence on Carbowax 20M) along with minor amounts of a 2 : 1 adduct ($M^+ = 158$ m.u.). It proved practical to isolate only the two major products by preparative g.l.c. but with behaviour characteristic of *ortho*-cycloadducts (*i.e.* having the cyclohexa-1,3-diene system), the adduct of shortest retention time was removed from the chromatogram by the treatment of the mixture with maleic anhydride although no crystalline compound could be obtained. Of the isolated isomers, that formed in the greater amount was assigned the 1,2-*para*-adduct structure (7) on the basis of its spectroscopic pro-



perties. In particular the ^1H n.m.r. spectrum showed four ethenyl protons and two bridgehead protons with chemical shifts and vicinal coupling constants expected for bicyclo[2.2.2]octa-2,5-diene systems:²⁸ the remainder of the spectrum comprised a doublet with further minor splittings for the terminal methylene protons and the resonances of the protons of the ring methylene protons which were coupled to the bridgehead proton at the higher field. The λ_{max} for this isomer of 216 nm and the observation of two C=C stretching modes in the i.r. spectrum are consistent with this assignment, as is the facile reversion to starting materials in the mass spectrometer.⁵

The second most abundant adduct was deduced to have arisen from *meta*-cycloaddition of one of the ethylenic moieties of the 1,2-diene to benzene. The chemical shifts and coupling constants for six of the ten protons were essentially identical to those of the benzene derived protons of *meta* benzene-ethylene cycloadducts.^{2,5,10,24} The two terminal methylene protons resonated at 4.85–4.90 p.p.m. and hence this adduct was deduced to have either structure (8) or (9). However, since from the ^1H n.m.r. spectrum it was evident that H-5 was coupled to two methylene protons ($J = 6$ and

ca. 0.5 Hz) as well as to H-1 and H-4, structure (8) was assigned to this product: this assignment of the more conjugated structure is substantiated by the u.v. spectrum of this isomer which had λ_{max} at 239 nm and hence has suffered a bathochromic shift of *ca.* 20 nm from that normally observed for vinylcyclopropane systems.²⁹ It proved impractical to monitor the allene photoaddition to benzene with time but it did appear that on prolonged irradiation of the system the relative proportion of (7) decreased and this we attribute to (7) reaching a photo-stationary state as may be expected for a *para*-cycloadduct, whereas linear formation of (8) with time continued for a much longer period.⁵ The alternative explanation for this observation is that (7) was converted into (8) by a di- π -methane rearrangement:³⁰ we reject this as no evidence was obtained from the irradiation of isolated (7) and (8) for their interconversion under the conditions of their formation. However, in order to assess more reliably the relative efficiencies of the *para*- and *meta*-cycloaddition reactions of 1,2-dienes to benzene, and whether the *para*-cycloadduct was a primary product and not derived from a photo and/or thermally labile *ortho*-cycloadduct [*i.e.* (10)],^{21,31} we examined the benzene-cyclonona-1,2-diene system. Irradiation of this 1,2-diene as a 10% (v/v) solution in benzene gave two 1 : 1 adducts ($M^+ = 200$ m.u. m.s.-g.l.c.) in an essentially time-invariant ratio of 1 : 6. This ratio was observed at the shortest feasible irradiation times and hence both are considered to be primary photochemical products. Preparative g.l.c. effected isolation of the major product essentially pure but because of the poor resolution under the various sets of chromatographic conditions examined, the minor isomer could in practise only be obtained with *ca.* 80% purity, the impurity being the major 1 : 1 adduct. From spectroscopic and analytical data, the major 1 : 1 isomer was assigned the *para*-1,2-cycloadduct structure (11). The ^1H n.m.r. spectrum showed the presence of four ethenyl protons in the 6.05–6.45 p.p.m. region which were coupled to the two protons, assigned bridgehead positions, at 3.75–3.95 and 3.30–3.55 p.p.m. (J 4.5 Hz). The one ethenyl proton triplet centred at 5.15 p.p.m. collapsed to a singlet on irradiation at 2.0 p.p.m. which thus located the allylic methylene proton resonance in the C_9 ring. The i.r. spectrum had absorptions at 1 660 and 1 600 cm^{-1} , typical of C=C stretching modes in a large-membered ring ethylene and a bicyclo[2.2.2]octa-2,5-diene respectively; the absence of a conjugated system was confirmed by the longest wavelength absorption at 220 nm. Unlike (7) and *para*-cycloadducts of alkenes and benzene,⁵ (11) appeared to be photostable but it did revert to starting materials in the injection block of a g.l.c. at *ca.* 300 °C. The ^1H n.m.r. spectrum of the 80% pure minor isomer, after subtraction of the resonances arising from (11), had the characteristic signals of *meta*-cycloadducts^{2,5,10,24} and was very similar to that of (8) but with absence of the terminal methylene resonance and the presence of a further ethenyl proton and 12 methylene proton resonances. The u.v. spectrum of this isomer had λ_{max} at

240 nm and hence of the two feasible regioisomer structures of the 1,2-*meta*-cycloadduct, (12) was assigned to the minor 1 : 1 adduct from irradiation of benzene and cyclonona-1,2-diene. The above reactions provide the first examples in which a hydrocarbon alkene undergoes *para* cycloaddition to benzene as the major process; with propene and *cis*-cyclononene, for example, *meta* 1 : 1-cycloadducts are formed exclusively with the former alkene¹⁴ and are the major products with the latter.^{9,10}

There has been much discussion concerning the factors which affect the relative efficiencies of the *ortho*- and *meta*-photocycloaddition processes of ethylenes to benzene and its simple derivatives: 7,9–14 the corresponding *para*-cycloaddition has been largely ignored presumably because it is observed in only a few systems and then with a relatively low efficiency.⁵ From orbital symmetry analyses of concerted cycloadditions of ethylenes to benzene it has been deduced that only the *meta*-process is 'allowed' from S_1 benzene,³² but such analyses do not apply when mixing with charge-transfer states is significant, and the intermediacy of exciplexes would relax the orbital symmetry restrictions.⁵ Indeed, it has been observed that as the electron donor or acceptor properties (as measured by ionisation potential of the ethylene) increase with respect to that of benzene, (*i.e.* as Δ I.P. increases) the relative efficiency of the formally 'forbidden' *ortho*-cycloaddition increases compared to that of the 'allowed' *meta*-reaction.^{9,10} As we have previously pointed out, however, it is important only to make correlations of ethylene ionisation potential with relative efficiency of addition within a series of structurally related addends.¹¹ The *para*-cycloaddition may be subject to the same considerations as those outlined above for the *ortho*-process in that the reaction may become relatively more favoured as the electron donor or acceptor properties of the ethylene increase but at present there is insufficient data on this reaction to allow meaningful deductions. The ionisation potential of allene is 9.69 eV, a value which, based on the original proposals concerning donor-acceptor properties of benzene-ethylene systems,⁹ would predict that processes 'forbidden' by orbital symmetry analyses would become observable, if not preferred. However, the danger of proposing a value of addend ionisation potential above and below which *ortho*- and/or *para*-cycloadducts may be expected is clearly illustrated here, since propene with

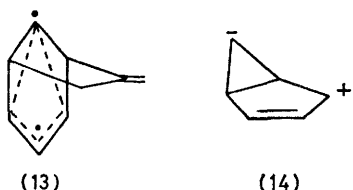
process and indeed why no *ortho*-cycloaddition was observed from the present systems.

We have previously described the regioselectivity of the *meta*-photocycloadditions of vinyl compounds to benzene³³ but it is interesting to note that formation of the 7-regio-isomer (8) is specific with 1,2-dienes and this has also been reported for the propene *meta*-addition.¹⁴ A reaction pathway involving initial *meta*-ethylene addition to yield (13) followed by formation of the ethenyl cyclopropane system²⁴ may be expected to yield a mixture of the 6- and 7-regio-isomers, whereas a mechanistic sequence in which prior *meta*-bonding in the benzene occurred to yield singlet prefulvene³⁴ or more probably the polarised species (14) could account for the observed specificity of addition of both the 1,2-diene and propene to benzene. The present results, therefore, substantiate the proposal that in order to account for all the *meta*-isomers from all systems it is necessary to consider dual mechanistic pathways, and that preferred can be influenced by steric and electronic effects of the addends.³⁵

The *meta* cycloadducts (8) and (12) were treated with potassium *t*-butoxide at both 20 and 80 °C in an attempt to promote the migration of the exocyclic ethylenic bond into the ring and hence yield semibullvalenes. The adducts were, however, inert to such treatment which either means that, as proposed earlier,³⁶ there is little 'aromatic' stabilisation in semibullvalene or that the carbanion was not formed.

The ionisation potential of keten is comparable to that of hydrocarbon 1,2-dienes³⁷ and so in view of the present results it was of interest to determine the photo-reactions of such compounds with benzene. Irradiation of keten in benzene gave, however, the keten dimer and low yields of toluene and cycloheptatriene, and dimethylketen produced a multicomponent mixture containing traces of cumene but specifically in neither case were 1 : 1 adducts with benzene detected.

(b) *Irradiation of Benzene with 1,3-Dienes.*—Previous studies with benzene and acyclic 1,3-dienes have generally yielded complex mixtures of products but as noted above the reaction may be moderated with iodine for synthetic purposes,^{20,21} and ground-state conformations may determine the adduct structure, with the *s-cisoid* conformer being the more reactive.¹⁹ These latter conclusions were based on studies of the photoaddition of benzene to *s-cisoid* 2,4-dimethylpenta-1,3-diene and 2,3-dimethylbuta-1,3-diene: the former gave the *para* 1,4-adduct (15) and a complex mixture of *meta*-adducts, but no diene dimers, whereas from the latter diene much polymer was produced and at least three diene dimers and seven 1 : 1 adducts. Formation of the adducts was considered to arise from singlet exciplexes, and of the diene dimers, from either a T_1 benzene-sensitised reaction and/or a triplet exciplex. In an attempt to simplify product mixtures and to obtain a clear decision of the importance of ground-state diene structure on reactivity and selectivity of the addend, we have examined the irradiation of benzene with the conformationally



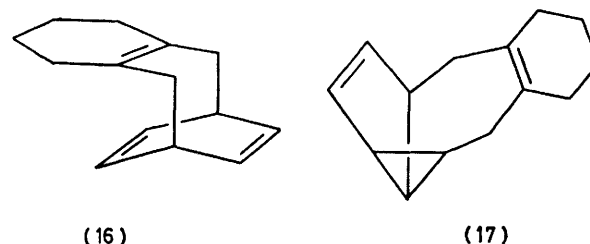
an ionisation potential of 9.73 eV yields *meta*-cycloadducts exclusively. Although structural differences between simple alkenes and 1,2-dienes are obvious, it is difficult to determine how these can promote the *para*-photocycloaddition from a very minor to the major

fixed 1,3-dienes 3-methylenecyclohexene and 1,2-dimethylenecyclohexene. Although both dienes are known to be photolabile^{38,39} such reactivity did not complicate the present study.

Irradiation of the 3-methylenecyclohexene–benzene system gave very low yields of a mixture of diene dimers ($M^+ = 188$ m.u.) and at least five 1:1 adducts ($M^+ = 172$ m.u.) (m.s.–g.l.c.) in an approximate ratio of 6:6:6:2:1 (elution sequence Carbowax 20M). The adducts were the major products at diene concentrations of 1.6M or less and their total quantum yield was *ca.* 0.003 for both 1:4 and 1:9 v/v solutions of the diene in benzene in the absence and presence of cyclohexane diluent. Chemical yields were also very low and irradiation for 72 h of 200 ml of solution gave less than 200 mg of distilled diene dimer–adduct mixture. Chromatographic separations were unsuccessful and no extraction of any adduct was achieved by either silver nitrate or mercuric acetate. Treatment of the adduct mixture with *N*-phenylmaleimide removed the adduct formed in *ca.* 10% yield but no solid product was obtained and the ^1H n.m.r. spectrum of the distilled components revealed the presence of protons on aromatic, ethenylic, terminal methylene, and saturated carbon atoms in a ratio of 1:5:2:16 respectively. Thus phenyl substitution of the diene as well as addition had occurred and, at least in some adducts, only the ring ethenyl bond has been involved, but no firm conclusions concerning adduct structures could be made. It is, however, worth noting that only for *para*-cycloaddition to the aromatic ring could both ethenylic moieties of this 1,3-diene be involved since the *meta*- and *ortho*-products would have the highly strained *trans*-cycloheptene and *trans*-cyclohexene systems respectively: it had been hoped that this feature may lead to a more selective addition reaction.

In contrast to 3-methylenecyclohexene, irradiation of 1,2-dimethylenecyclohexane mixtures with benzene gave essentially only two products under conditions where either the arene or the diene absorbed most of the radiation. Mass spectral analysis of the two products showed that both were 1:1 adducts of the starting materials and that the major unlike the minor, fragmented readily under electron impact back to benzene and the diene. At diene concentrations up to 50 mol % the ratio of the adducts was *ca.* 1:2 (elution sequence on Carbowax 20M) and the total quantum yield was 0.06 but at higher diene concentrations, for example 80 mol % at which the diene is absorbing *ca.* 90% of the incident radiation, the adducts were formed in equal amounts and the quantum yield was reduced by a factor of two. Neither adduct reacted with *N*-phenylmaleimide, thus demonstrating in both isomers the absence of a 1,3-diene moiety as is present in *ortho*-cycloadducts of benzene, but the major product from equimolar mixtures of the reactants was extracted from a pentane solution of the photoproduct by shaking with aqueous silver nitrate. The precipitated solid afforded the major 1:1 adduct as colourless needles (m.p. 42.5 °C) on treatment with

ammonia. From spectroscopic and analytical data of the crystalline major 1:1 adduct the *para*-1,4-adduct structure (16) was assigned. The ^1H n.m.r. spectrum showed the presence of four ethenyl protons in the 5.75–6.20 p.p.m. region resonating as overlapping doublets

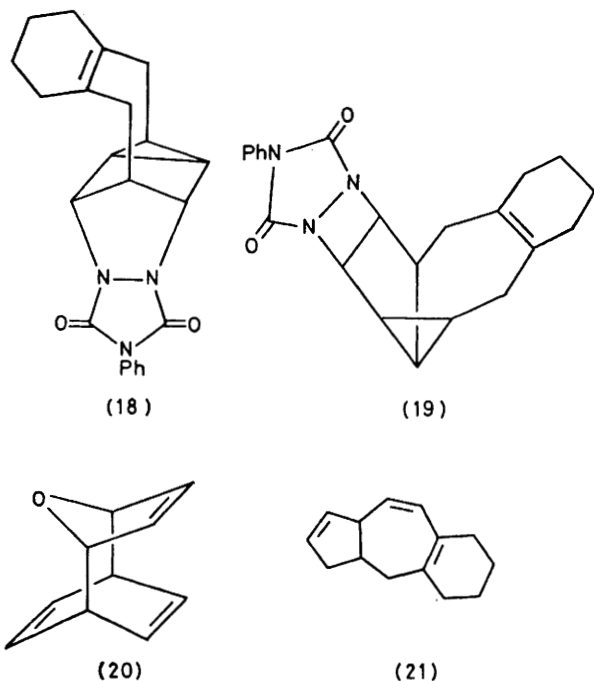


which were coupled (J 4 Hz) to the two protons, assigned to the bridgehead positions at 2.60–3.10 p.p.m. These resonances were deduced to be benzene-derived as the spectrum of the corresponding C_6D_6 -1,2-dimethylenecyclohexane adduct showed simply resonances at 2.20–2.50 (4 H), 1.60–2.00 (4 H), and 1.20–1.60 p.p.m. (4 H) which also completed the spectrum of that of the hydrocarbon adduct but in this latter case, the resonance at 2.20–2.50 p.p.m. was further split by coupling to the bridgehead protons.

The pentane solution from which (16) was extracted yielded an adduct mixture enriched in the minor isomer and subsequent preparative g.l.c. gave samples of this latter product essentially free from (16). The minor 1:1 adduct of benzene and 1,2-dimethylenecyclohexane was assigned the *meta*-1,4-adduct structure (17) from spectroscopic and analytical data. In particular, the ^1H n.m.r. spectrum showed the presence of but two ethenyl protons and no terminal methylene protons, hence both ethylenic moieties of the 1,3-diene have been involved in the reaction: the benzene-derived protons in the spectrum were again assigned by comparison with the ^1H n.m.r. spectrum of the corresponding C_6D_6 adduct. Comparison of these spectra with those of *meta*-cycloadducts of benzene and ethylenes showed that although the chemical shift difference of the two ethenyl protons in (17) was less than in many previous cases, the overall multiplicities and resonance positions were those expected. Consistent with the structural assignments, (16) and (17) reacted with 4-phenyl-1,2,4-triazoline-3,5-dione to yield crystalline 1:1:1 adducts ($M^+ = 361$ m.u.), which are assigned structures (18) [m.p. 152–154 °C (decomp.)] and (19) [m.p. 164–166 °C (decomp.)] respectively on the basis of spectroscopic and analytical data, and the reaction of this dienophile with bicyclo[2.2.1]hepta-2,5-diene⁴⁰ and the *meta*-cycloadduct of *cis*-cyclo-octene and benzene: the minor adduct also gave minor amounts of a 1:1:1 adduct ($M^+ 314$ m.u.) when heated with tetracyanoethylene in dichloromethane.³ Evidence was obtained from ^1H n.m.r. spectroscopy that a weak ground-state complex may exist between benzene and 1,2-dimethylenecyclohexane, but the absorption spectrum of addend mixtures was additive of the components and, although

the diene quenched the benzene fluorescence at a near diffusion-controlled rate, no longer wavelength exciplex emission was observed.

In view of the facile thermal and photochemical Cope rearrangements of the *para*-2,5-photocycloadduct (20) of benzene and furan,⁴¹ it was of interest to determine the labilities of (16) and (17) to heat and light since both adducts may, in principle, yield isomers by Cope rearrangements. The adducts were essentially stable



under their conditions of formation although slow reversion of (16) into starting materials was observed in benzene solution, and heating their solutions at 110 °C caused no detectable change in their ¹H n.m.r. spectra. At temperatures of *ca.* 250 °C, however, (17) gave the isomer (21) which is presumed to have arisen by the well-known 1,5-sigmatropic shift route,⁴² whereas (16) underwent retro-addition to starting materials as well as yielding tetralin and butadiene. This latter pyrolysis has been examined in further detail and has been accounted for by a sequence involving intramolecular and retro Diels-Alder reactions.⁴³ The mechanism was supported by the pyrolysis of the *para*-1,4-photoadduct, obtained from this diene and hexadeuteriobenzene, to 2,3-di-deuteriobutadiene and tetralin with four aryl deuteriums.

Thus we have shown that a conformationally fixed *cisoid* diene is more reactive in photoaddition to benzene than a conformationally *trans*-diene (quantum yield ratio *ca.* 20 : 1 respectively). It is also most significant that the reactions of the former diene were very selective whereas the latter, despite certain adducts being most unfavoured from strain considerations and hence limiting the modes of reaction, gave a complex mixture of adducts as well as diene dimers.

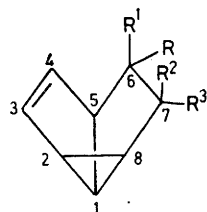
Unfortunately not all *cisoid* dienes were as obliging as

1,2-dimethylenecyclohexane in this reaction as our preliminary studies with cyclo-octa-1,3-diene and cyclopentadiene showed. Thus from irradiation of benzene with the former diene traces of 1 : 1 adducts were only detected (m.s.-g.l.c.) when (a) the concentration of diene in benzene was <0.4% v/v, (b) a 1% solution of the diene in benzene was degassed under oxygen, or (c) the solutions were diluted at least twofold in an inert solvent. Hence 1 : 1 adducts could be formed under conditions in which the diene does not absorb the incident radiation, or *T*₁ benzene was quenched by oxygen or its concentration reduced, but in all cases the amounts of product mixtures obtained were too small to contemplate isolation and separation of the components. Cantrell has reported that irradiation of 5 : 1 mixtures of 'xylene' and cyclopentadiene yields a *meta*-1,4-adduct as the major product.⁴⁴ We observed five 1 : 1 adducts (m.s.-g.l.c.) from benzene and cyclopentadiene but only when the diene concentration was 1.0M or less in the arene. Assessment of the relative proportions of the adduct was complicated by their thermal labilities and interconversions but using low injection block g.l.c. analysis a ratio of approximately 4 : 4 : 10 : 1 : 10 (elution sequence Carbowax 20M) was determined. The yields of products were again very low and did not encourage their separation.

(c) *Irradiation of Benzene with 1,4-Dienes.*—Since both 1,2- and 1,3-dienes had given *para*-cycloaddition to benzene as the major photoprocess, it was of interest to examine 1,4-dienes in this reaction in order to assess if such compounds would behave simply as alkenes (*e.g.* propene¹⁴) and yield only *meta*-cycloadducts, and in such additions if the second ethenylic bond would affect the stereo- and/or regio-selectivity of the process. We chose for this study penta-1,4-diene, cyclohexa-1,4-diene, and bicyclo[2.2.1]hepta-2,5-diene since with the spread of ionisation potential of almost 1 eV the importance of relative electron donor-acceptor properties of the starting materials may be assessed.

Irradiation of penta-1,4-diene (I.P. = 9.58 eV) in benzene solution gave a 1 : 8 : 5 mixture (elution sequence Apiezon L) of three 1 : 1 adducts (*M*⁺ = 146 m.u. m.s.-g.l.c.) of the starting materials. The ratio of the products was not significantly affected by irradiation time, atmosphere, or diene concentration and since none of the adducts reacted with common dienophiles nor was absorption from a tetraene evident in the ultraviolet-visible spectrum of the irradiated solution,⁴⁵ it was deduced that no *ortho*-cycloaddition to the benzene ring had occurred. The major 1 : 1 adducts were separated by preparative g.l.c.: the one of greater abundance was obtained essentially pure whereas the minor isomer persistently contained 7–10% of the major isomer. From the spectroscopic properties of these adducts and their comparison with those of adducts of known structure,^{2,5,10,24} both are assigned *meta*-cycloadduct structures. The longest wavelength absorptions of the major and minor adducts in cyclohexane were at 238 and 231 nm respectively and thus each had a more extensive

conjugation than that solely of the ethenyl cyclopropane chromophore of *meta*-cycloadducts which absorbs at 220 nm or at shorter wavelengths.²⁹ From this feature we deduced that both of the present *meta*-cycloadducts have *endo*-stereochemistry as this allows through-space interaction between the two chromophores. Further it was observed that while the major 1 : 1 adduct was thermally stable up to 300 °C, the minor *meta*-product isomerised under the same conditions *via* a 1,5-sigmatropic shift; thus in view of the known differential thermal labilities of *meta*-adduct isomers,⁴² the major and minor *meta*-products from penta-1,4-diene and benzene were assigned structures (22) and (23) respectively. These assignments



(22) $R = R^1 = R^3 = H, R^2 = CH_2 - CH = CH_2$

(23) $R = R^2 = R^3 = H, R^1 = CH_2 - CH = CH_2$

(28) $R = R^3 = H, R^1 - R^2 = CH_2 - CH = CH - CH_2$

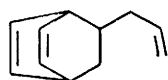
(29) $R^1 = R^2 = H, R - R^3 = CH_2 - CH = CH - CH_2$

were substantiated by detailed examination of the ¹H n.m.r. spectra and spin-decoupling experiments. Thus the chemical shifts, multiplicities, and integrations of the proton resonances for both isomers were entirely consistent with the presence of an ethenylcyclopropane and a vinyl group. Further, the appearance of the broad triplet and quartet at *ca.* 3.0 and 2.6 p.p.m. are characteristic of the H-5 and H-1 resonances respectively in *meta*-cycloadducts. The triplet nature of H-5 in (22) suggested the presence of the *exo*-proton H-6 since in *meta*-cycloadducts H-5 couples equally with H-1 and H-6 (6 Hz) but not H-6' as the dihedral angle is near 90°. Proton H-6 was located in the broad resonance at 2.3–1.8 p.p.m. by irradiation of H-5 and H-6'. The high-field doublet centred at 1.4 p.p.m. was assigned to H-6': the chemical shift and coupling constant were in close agreement with the values for the analogous proton in the 7,7-disubstituted benzene-isobutene adduct.¹⁰ That no further splitting of the H-6' resonance was observed is consistent with the deduced stereochemistry in (22), since the *exo*-proton at C-7 subtends a dihedral angle of 90°. The appearance of the H-5 signal in (23) was again a triplet and this established the presence of an *exo*-proton at C-6. Spin decoupling allowed the location of its position and since this resonance did not show the expected large coupling with a geminal proton it was concluded that the *endo*-position at C-6 was substituted: thus the stereo- and regio-chemistries of this adduct deduced from u.v. spectroscopy and its thermal lability, were confirmed. The minor 1 : 1 adduct from this reaction could not be isolated sufficiently pure for spectral analysis. However, from its ready

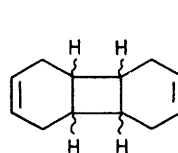
fragmentation in the mass spectrometer⁵ and pyrolysis to starting materials but lack of reaction with common dienophiles, we tentatively assign the *para*-cycloadduct structure (24) to this product. Quantum yields were determined for 1.0M-benzene and 1.75M-diene in iso-octane solution to be 0.08 for the total *meta*-cycloaddition and 0.006 for the formation of the minor product.

Despite the *endo*-stereochemistry of (22) and (23) and interaction of the ethenyl chromophores, neither adduct underwent acetone-sensitised intramolecular (2 + 2) cycloaddition: the former photolysed to starting materials whereas the latter was remarkably photostable. Photostability of *meta*-cycloadducts has been related to the presence of substituents which are able to obstruct the approach of a sensitizer molecule,⁴⁶ and this consideration may explain the differing labilities of (22) and (23) since from molecular models, the former appears to be a compact molecule with restricted rotation of the allyl group whereas (23) can adopt a more open structure.

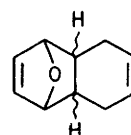
Irradiation of benzene-cyclohexa-1,4-diene (I.P. = 8.82 eV) mixtures gave six products whose ratios were time independent but varied markedly with reactant concentrations. The products were shown by mass spectral analysis of g.l.c. fractions to be three diene dimers and three 1 : 1 adducts of the starting materials. As with other systems^{10,47} the relative yields of the adducts compared to that of the dimers were greatly increased at high diene concentrations or by the use of cyclohexane as diluent, observations consistent with a *T*₁ benzene-sensitised route to the diene dimers and *S*₁ benzene leading to adduct formation. The relative ratio of the adducts formed in the presence of cyclohexane was *ca.* 1 : 1 : 1. The six products from the reaction were separated by preparative g.l.c. The spectroscopic properties of each dimer were very similar and in particular the ¹H n.m.r. spectra all had a ratio of ethenyl protons to protons on a saturated carbon atom of 1 : 3 which suggested that the dimers were derived from (2 + 2) cycloaddition to yield the cyclobutane derivatives (25). In the present study a detailed analysis of



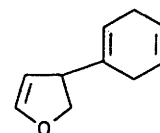
(24)



(25)



(26)



(27)

the stereochemistry of the dimers was not attempted but as in the case of the benzene-sensitised cyclohexene dimerisation,¹⁰ that *three* cyclobutane dimers are formed, tends to argue against the involvement of a highly reactive *trans*-ethylene whereas a triplet species would be more likely to react non-selectively. Irradiation of a 10% (v/v) solution of the diene in benzene containing 10% furan essentially quenched diene dimer formation and gave only a 1 : 1 adduct of cyclohexa-1,4-diene and furan which was not formed in the absence of benzene and hence furan clearly intercepted the dimer precursor. The

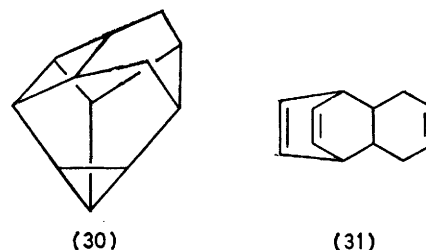
spectroscopic data of the furan–diene adduct discounted a 2,5-, 1,2-adduct structure (26) with either *cis*- or *trans*-ring junction and the absorption maximum at 215 nm showed the absence of a conjugated structure. On the basis of the spectral data and their comparison with those of the major furan–cyclohexene adduct,¹⁰ structure (27) is assigned to the product from benzene-sensitised addition of cyclohexa-1,4-diene to furan.

There are only two possible *meta*-1,2-cycloadducts of benzene and cyclohexa-1,4-diene and the spectra of two of the separated 1 : 1 adducts were consistent with structures (28) and (29). The differentiation between the two was made from the absorption spectra: thus, the adduct with λ_{max} of 237 nm was assigned the *endo*-structure (28) whereas the other had λ_{max} at 226 nm and was thus deduced to be the *exo*-isomer (29). The ¹H n.m.r. spectrum of both isomers had ratios of ethenyl to saturated proton resonances of 4 : 10 and although the characteristic appearance of the ethenyl protons of *meta*-cycloadducts was masked to some extent by the additional two ethenyl proton resonances of the cyclohexene, signals typical of H-1 and H-5 were clearly evident. In the adduct assigned the *exo*-structure (29) the H-5 resonance was a double doublet ($J_{1,5}$ 6 Hz, $J_{4,5}$ 2 Hz) and coupling with a proton on C-6 was absent thereby indicating the *exo*-stereochemistry for this compound as typical coupling between *exo* H-6 and H-5 is *ca.* 6 Hz and that between *endo* H-6 and H-5 is zero or nearly so. The H-5 resonance in the isomer assigned (28) showed couplings with H-1, H-4, and *exo* H-6 and hence *endo*-stereochemistry was assigned to this *meta*-cycloadduct. Consistent with these conclusions, the adduct assigned (28) was thermally stable at 250 °C whereas the *exo*-adduct was converted into a shorter retention time isomer.²⁹ Further, whereas (29) was essentially stable to acetone-sensitised irradiation, the *endo*-compound (28), unlike (22) and (23) from benzene and penta-1,4-diene, gave an isomer (M^+ 158 m.u.) of shorter retention time which had no resonances at lower field than 3.0 p.p.m. and hence in which both ethylenic bonds of (28) had reacted: from these data and by analogy with the intramolecular photocyclisation of the dechlorinated *meta*-cycloadduct of benzene and 3,4-dichlorocyclobutene,⁴⁸ the 'caged' structure (30) is tentatively proposed for the present photoisomer of (28). The *endo*-*meta*-adduct usually predominates in stereoisomeric mixtures and from many systems is the exclusive product.⁴⁹ It was, therefore, surprising that from the benzene–cyclohexa-1,4-diene system where it may have been expected that maximum interaction of the addends would be achieved in an *endo*-sandwich approach, the ratio of *exo* to *endo* was 1 : 1 but indeed the photoreactions of cyclohexene itself with benzene are anomalous since in this case only trace amounts of product are formed.¹⁰

Interestingly both (28) and (29) showed a facile retro-Diels–Alder reaction in the mass spectrometer with the loss of butadiene, and the C_8H_8^+ ion had an abundance of *ca.* 50–60% of the base ion of 92 m.u. Attempts to use the thermal and photochemical retro-Diels–Alder reaction

of *meta*-cycloadducts as a route to semibullvalene were unsuccessful and have been described elsewhere.¹¹

It proved extremely difficult to free the third 1 : 1 adduct of benzene and cyclohexa-1,4-diene from diene dimers and the *meta*-cycloadduct (28). However, this component reverted to starting materials readily on electron impact (base ion 80 m.u.),⁵ was inert to common dienophiles, and its maximum absorbance was at 220 nm. These data indicated that this product had the *para*-cycloadduct structure (31) and this was supported by



the ¹H n.m.r. spectrum which had resonances at 6.0–6.3 p.p.m. with primary and secondary couplings of 4.5 and 3.0 Hz which are typical for ethenyl protons of bicyclo[2.2.2]octa-2,5-diene systems,²⁸ a broad multiplet centred at 6.4 p.p.m. (cyclohexene protons), and resonances of protons on saturated carbon atoms between 3.0 and 1.0 p.p.m.: integration of the spectrum was inexact because of the impurities referred to above. *para*-Cycloaddition of alkenes to benzene is, with the exception of 1,2-dienes, a relatively minor process and the competing reaction to *meta*-cycloaddition is generally either the *ortho*-process or, with 1,1-dimethylethylenes, an 'ene'-type reaction.¹⁰ Hence it is all the more significant that in the case of 1,4-dienes and benzene that no evidence for formation of *ortho*-cycloadducts was observed but, instead, the corresponding *para*-process competes with *meta*-cycloaddition. Further, the only other system where no *ortho*-product was reported but where *meta*- and *para*-cycloaddition occurred was that involving benzene and cyclobutene,²⁸ but the common features of this and the present systems which may direct the photoprocess away from *ortho*- to *para*-cycloaddition are not obvious.

In view of the reactions described above with benzene and the 1,4-dienes and those reported for bicyclo[2.2.1]hept-2-ene as addend,⁴⁷ it was surprising to observe that under a variety of experimental conditions and a wide range of reactant proportions, the benzene–bicyclo[2.2.1]hepta-2,5-diene system was essentially inert to 254 nm radiation and, in particular, no evidence was obtained for formation of 1 : 1 adducts or dimers of the diene. In contrast, this diene is reported to undergo photoreaction with hexafluorobenzene but unlike the addition of *cis*-cyclo-octene to this arene,⁵⁰ only products of *ortho*-cycloaddition are observed.⁵¹

To summarise, we have shown that 1,2-dienes are unique among ethenylic systems as they yielded *para*-1,2-cycloadducts with benzene as the major mode of

reaction. The *meta*-cycloaddition from these systems was regiospecific and may be accounted for by a mechanism involving prior arene rearrangement followed by 1,2- concerted attack of one of the ethenyl moieties. 1,2-Dimethylenecyclohexane underwent selective reaction with benzene to give only the 1,4-*meta*- and *para*-cycloadducts whereas from more flexible systems and the fixed *trans*-diene, 3-methylenecyclohexane, complex mixtures resulted. 1,4-Dienes reacted with photoexcited benzene in a manner analogous to simple alkenes, although from these dienes evidence was obtained for 1,2-*para*-cycloaddition to benzene rather than the more usual competing process of *ortho*-cycloaddition. For the 1,2- and 1,4-dienes we have studied, there was no correlation apparent between addend ionisation potential and mode of photocycloaddition.

EXPERIMENTAL

Mixtures of the addends with and without cyclohexane diluent were sealed in quartz tubes of varying capacities and subjected to the radiation from low-pressure 15-W Hanovia mercury-arc lamps. Temperatures of the experiments were maintained at 20–25 °C and the progress of the reaction was monitored by g.l.c. Both for analytical and preparative g.l.c. the column packing used for the separations was 15% Carbowax 20M on Universal B support (ex Phase Separations Ltd.): the only exception to this was for the benzene-penta-1,4-diene photoproducts which were more efficiently separated using columns packed with 8% Apiezon L plus 2% KOH on Universal B support. All column materials were stainless steel, the analytical columns were 0.2 cm i.d. and 200 cm long and the preparative columns comprised multiples of units 0.7 cm i.d. and 100 cm long. The standard work-up procedure involved removal of the reactants from the irradiated mixtures under vacuum at < 40 °C, analysis of the oil by g.l.c. followed by vacuum distillation (0.05 mmHg) of the products and their separation by preparative g.l.c. The effect of atmosphere on reactions was investigated for addend mixtures under air and following flushing with the appropriate gas (*i.e.* N₂ or O₂) for at least 1 h prior to irradiation. Acetone-sensitised irradiations of the adducts were carried out in Pyrex tubes using Hanovia medium-pressure 100-W mercury-arc lamps and the solutions were nitrogen degassed. Unless otherwise stated, ¹H n.m.r. spectra were recorded at 100 MHz in CCl₄ solutions with SiMe₄ as internal standard.

Irradiation of Benzene and 1,2-Dienes.—(a) *Propa*-1,2-diene (*allene*). The diene was bubbled slowly into the irradiation cell containing benzene (100 ml) which had previously been purged with dry nitrogen, until a 5% increase in volume was noted. The solution was irradiated for 24 h. The diene (*ca.* 4 ml) was recovered and the product (*ca.* 0.5 ml) was bulked with that from several other experiments for further treatment. In view of the small quantities of product obtainable from this reaction it proved only realistic to isolate mixtures enriched in each isomer by preparative g.l.c. The purities of such fractions were 85–90% in (7) or (8) with the impurity being (8) and (7) respectively.

Compound (7) had the following spectral characteristics: λ_{max} (n-hexane) 216 nm; ν_{max} (liquid smear) 3 050, 2 950, 1 650, 1 590, and 710 cm⁻¹; δ 6.1–6.4 (4 H, t, $J_{\text{vic}} = J_{\text{allylic}}$ 3.7 Hz), 4.5br (1 H, s), 4.7br (1 H, s), 3.7–4.0 (1 H, m),

3.5–3.7 (1 H, m, $J_{\text{CH}_2\text{-allylic}}$ 2.5 Hz), and 1.9–2.0 (2 H, split d, $J_{\text{CH}_2\text{-C=CH}_2}$ 1 and 2 Hz).

Compound (8) had the following spectral characteristics: λ_{max} (n-hexane) 238 nm; ν_{max} (liquid smear) 3 050, 2 950, 1 650, 1 590, 1 340, 880, 740, and 720 cm⁻¹; δ 5.50–5.60 (1 H, dd, J 5.5 and 2.0 Hz), 5.30–5.45 (1 H, dd, J 5.5, 2.3, and 1.5 Hz), 4.85–4.90 (2 H, d, J 1.0 Hz), 3.02–3.20 (1 H, t of d, J 6 and 3 Hz), 2.65–2.95 (1 H, m, J_{gem} 13 Hz, $J_{\text{CH}_2\text{-C=CH}_2}$ 6 Hz), 2.50–2.70 (1 H, q, J 6 Hz), and 1.85–2.05 p.p.m. (3 H, three overlapping resonances, J 6.0 and 0.5 Hz).

(b) *Cyclonona*-1,2-diene.⁵² A 10% (v/v) solution (50 ml) of the diene in benzene irradiated for 24 h gave a pale yellow distilled oil (0.2 g). Preparative g.l.c. gave (11) essentially pure and (12) with 80% purity, the impurity being (11) [Found for (11): C, 89.75; H, 10.35. C₁₅H₂₀ requires C, 90.0; H, 10.0%].

Compound (11) had the following spectral characteristics: λ_{max} (n-hexane) 220 nm; ν_{max} (liquid smear), 3 050, 2 950, 2 850, 1 660, 1 600, 1 450, and 720 cm⁻¹; δ 6.05–6.45 (4 H, m, J 7 and 4.5 Hz), 5.0–5.25br (1 H, t, J 8 Hz), 3.75–3.95br (1 H, m, J 5.5 and 2.0 Hz), 3.30–3.55br (1 H, m, J 5.5 and 2.0 Hz), 1.9–2.1br (3 H, d, J 2.3 Hz), and 1.0–2.0br p.p.m. (10 H, s).

Compound (12) had λ_{max} (n-hexane) at 240 nm. The other spectroscopic features were closely similar to those of (8) but with the absence of a terminal methylene proton resonance, and the presence of three ethenyl protons in the 5.4–5.7 p.p.m. region and a broad singlet resonance at 1.0–2.0 p.p.m. for the nine-membered ring methylene protons.

Irradiation of Benzene with Keten and Dimethylketen.—Keten was bubbled into azeotropically dried benzene (100 ml) in the irradiation cell until a 3% increase in volume was observed. The mixture was irradiated for 70 h and the brown solution afforded a dark brown oil (*ca.* 0.5 ml) which contained keten dimer and traces of toluene and cycloheptatriene: the latter were identified by g.l.c. and combined m.s.–g.l.c.

Dimethylketen (5 ml) was distilled under nitrogen into benzene (100 ml) in the irradiation cell. After irradiation for 40 h and work-up, an orange liquid (*ca.* 1 ml) was obtained. This was a complex mixture containing seven major products none of which had M^+ values consistent with a 1 : 1 adduct; small amounts of cumene were, however, detected.

Irradiation of Benzene with 1,3-Dienes.—(a) *3-Methylenecyclohexene*. Irradiation of a 1.6M-solution (200 ml) of the diene in benzene for 72 h gave less than 0.2 g of a distilled colourless oil. Of the major adducts, three showed facile fragmentation to starting materials in the mass spectrometer whereas the fourth had a base ion of 91 m.u. The ¹H n.m.r. spectrum (60 MHz) of the mixture showed resonances at 7.0–7.3, 5.4–5.8, 4.5–4.7, and 1.4–3.0 p.p.m. in a ratio of 1 : 5 : 2 : 16 respectively. Attempts to obtain separations and solid products from ethereal solutions of *N*-phenylmaleimide, aqueous or methanolic solutions of silver nitrate, and methanolic solutions of mercuric acetate failed; only in the first case was any product removed from the chromatogram.

(b) *1,2-Dimethylenecyclohexane*.—The adduct mixture (*ca.* 1 g) from irradiation (48 h) of a 10% (v/v) solution (100 ml) of the diene in benzene in pentane (15 ml) was shaken with 30% aqueous silver nitrate (15 ml) for 5 min. The pentane layer was combined with the pentane washings (2 × 10 ml) of the aqueous layer in which the silver nitrate–(16) complex

was suspended. Removal of the pentane at water-pump pressure gave *ca.* 0.3 g of an oil containing essentially only (17). Combined products from four such extractions were vacuum-distilled and further purified by preparative g.l.c. to give (17) essentially free from (16). The spectral properties were as follows: λ_{max} (cyclohexane) 220 nm; ν_{max} (liquid smear) 3 080, 3 040, 2 840, 1 640, 1 450, 1 375, 888, 780, and 725 cm^{-1} ; δ (60 MHz) 5.50—5.65br (2 H, s), 3.0—3.3 (1 H, m), 2.10—2.45 (3 H, m), 1.75—2.10br (7 H, m), and 1.30—1.75br p.p.m. (5 H, m); $M^+ = 186$ m.u. (Found: C, 90.05; H, 9.8. $\text{C}_{14}\text{H}_{18}$ requires C, 90.32; H, 9.68%).

The precipitate in the aqueous layer was filtered off to give a white solid (0.5 g) which slowly turned grey in light and charred at temperatures above 130 °C. Treatment of the solid with 2M-aqueous ammonia (25 ml) and extraction with carbon tetrachloride gave a solution of (16). Removal of the carbon tetrachloride gave (16) as white needles (m.p. 42.5 °C). The spectral properties were as follows: λ_{max} (cyclohexane) 215 nm; ν_{max} (liquid smear) 3 080, 3 015, 3 000, 2 900, 1 640, 1 445, 1 395, 1 290, 1 005, 845, 780, 710, and 665 cm^{-1} ; δ (60 MHz) 5.75—6.20 (4 H, overlapping ds, J 4.0 Hz), 2.60—3.10 (2 H, m), 2.20—2.50br (4 H, s), 1.60—2.00 br (4 H, s), and 1.20—1.60br p.p.m. (4 H, t, J 3.0 Hz); $M^+ = 186$ m.u. (Found: C, 90.1; H, 9.85. $\text{C}_{14}\text{H}_{18}$ requires C, 90.32; H, 9.68%).

Treatment of the distilled mixture (0.5 g) with a saturated solution of 4-phenyl-1,2,3-triazoline-3,5-dione in methylene chloride (5 ml) produced initially (after *ca.* 0.2 g of solid dienophile had been added) a gummy white solid which was recrystallised from methylene chloride, $M^+ = 361$ m.u., m.p. 164—166 °C (decomp.), ν_{max} 1 770, 1 710, and 770 cm^{-1} ; δ values (CD_2Cl_2) for only five aryl protons centred at 7.3 p.p.m. and eighteen protons on saturated carbon (1.0—3.0 p.p.m.) (Found: C, 72.95; H, 6.55; N, 11.1. $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2$ requires C, 73.13; H, 6.37; N, 11.63%). This derivative was that of (17), for the solution after removal of the solid contained only (16) by g.l.c. Addition of further amounts of the triazoline to the solution gave a further solid (0.2 g), $M^+ = 361$ m.u., m.p. 152—154 °C (decomp.), ν_{max} 1 770, 1 710, and 770 cm^{-1} ; again the ^1H n.m.r. spectrum (CD_2Cl_2) showed only protons on aryl carbons and saturated carbons (Found: C, 72.9; H, 6.6; N, 11.4. $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_2$ requires C, 73.13; H, 6.37; N, 11.63%).

The hexadeuterio-adducts of (16) and (17) from 1,2-dimethylcyclohexane and C_6D_6 were prepared and separated as described above. Spectral changes were consistent with the assignments. Decomposition of hexadeuterio- (16) to 2,3-dideuteriobutadiene, tetradeuteriotetralin, and 1,2-dimethylenecyclohexane and C_6D_6 was accomplished by injecting 40 μl of a 20% (w/w) solution of the adduct in benzonitrile into the injection port at 250 °C of the preparative g.l.c.: the pyrolysis was allowed to proceed for 2 min and the carrier gas was then flushed through the port and the products separated and collected.

Irradiation of Benzene with 1,4-Dienes.—(a) *Penta-1,4-diene.* Irradiation of a 10% (v/v) solution (55 ml) of penta-1,4-diene in benzene gave a pale yellow oil (0.5 g). The procedure was repeated several times and the vacuum-distilled oil was separated by preparative g.l.c. The i.r. spectra (liquid smear) of (22) and (23) were very similar and had ν_{max} at 3 075, 3 045, 3 025, 2 970—2 860, 1 640, 1 440, 995, 910, and 710 cm^{-1} ; δ values for (22) were at 5.4—6.2 (1 H, m), 5.3—5.7 (2 H, m), 4.6—5.2 (2 H, m), 2.9—3.2br (1 H, m), 2.4—2.9 (1 H, q, J 6 Hz), 1.8—2.8 (4 H, m), 1.6—1.8 (2 H, four-line resonance), and 1.3—1.6 p.p.m. (1 H, d, J 12 Hz);

δ values for (23) were at 5.4—6.2 (1 H, m), 5.3—5.7 (2 H, m), 4.6—5.2br (2 H, t), 2.8—3.1br (1 H, t), 2.2—2.6 (1 H, q, J 6 Hz), and 1.0—2.8 p.p.m. (7 H, series of multiplets). [Found for (22): C, 90.15; H, 9.71. $\text{C}_{11}\text{H}_{14}$ requires C, 90.41; H, 9.59%].

(b) *Cyclohexa-1,4-diene.* A 20% (v/v) solution (55 ml) of cyclohexa-1,4-diene in benzene was irradiated for 24 h and gave a pale yellow oil (*ca.* 1 ml) containing the dimers and 1:1 adducts in approximately equal amounts. The procedure was repeated several times, the oil was vacuum-distilled, and the products separated by preparative g.l.c. The dimers had a ratio of *ca.* 1:3:3 (elution sequence Carbowax 20M): the first two were sticky solids at room temperature whereas the third was an oil. The u.v. spectrum (cyclohexane) of each dimer had only end-absorption beyond 220 nm and ν_{max} at 3 030, 1 625, and 665 cm^{-1} . The δ values for the dimers were respectively 5.5—5.9br (4 H, s) and 1.5—2.8br (12 H, s); 5.9—6.05br (4 H, s) and 1.9—2.2br (12 H, s); and 5.5—5.85br (4 H, s), 1.8—2.2br (8 H, s), and 1.2—1.8br p.p.m. (4 H, s).

Irradiation of a solution of furan (2.5 ml) and cyclohexa-1,4-diene (2.5 ml) in benzene (45 ml) for 18 h produced the 1:1 adducts and the furan-cyclohexa-1,4-diene adduct ($M^+ 148$ m.u., base ion 80 m.u.) which was isolated from the mixture by preparative g.l.c. Compound (27) had ν_{max} (liquid smear) 3 020 and 1 620 cm^{-1} and δ values at 6.4—6.6 (1 H, dd, J 6 and 2 Hz), 6.2br (1 H, s, J 0.5), 5.8—6.0 (1 H, dd, J 6 and 2 Hz), 5.5—5.7br (2 H, d, J 2.5 Hz), 4.8br (1 H, s), 4.4br (1 H, s), and 1.4—2.8 (5 H, series of m's) (Found: C, 80.95; H, 8.35. $\text{C}_{10}\text{H}_{12}\text{O}$ requires C, 81.08; H, 8.11%).

The spectra of (31) are outlined in the text. Compound (28) had the following spectral features: λ_{max} (cyclohexane) 237 nm; ν_{max} (liquid smear), 3 040, 3 020, 1 650, 745, and 730 cm^{-1} ; δ 5.3—5.9br (4 H, m), 2.8—3.2br (1 H, m), 2.4—2.8 (1 H, q, J 6 Hz), and 1.5—3.2 p.p.m. (8 H, series of m's) (Found: C, 90.95; H, 9.05. $\text{C}_{12}\text{H}_{14}$ requires C, 91.14 H, 8.86%). Compound (29) had the following spectral features: λ_{max} (cyclohexane) 226 nm; ν_{max} of the significant structural isomers as for (28) above; δ 5.2—5.8 (4 H, m, highfield half of AB q discernible, J 5 and 2 Hz), 2.7—2.9 (1 H, t of d, J 6 and 2 Hz), 2.3—2.7 (1 H, q, J 6 Hz), and 1.0—2.9 p.p.m. (8 H, series of m's) (Found: C, 91.35; H, 8.7. $\text{C}_{12}\text{H}_{14}$ requires, C, 91.14; H, 8.86%).

Irradiation of the distilled adduct mixture (2g) in acetone (40 ml) under nitrogen in a Pyrex tube with a 100-W medium-pressure mercury-arc lamp produced a new short retention time isomer ($M^+ 158$ m.u.) solely at the expense of the *meta*-cycloadduct (28). The reaction was followed by g.l.c. (Carbowax 20M) and was judged to be complete within 24 h. Product isolation was by preparative g.l.c.: the photoisomer was tentatively assigned structure (30) (see text).

(c) *Bicyclo[2.2.1]hepta-2,5-diene.* This diene was irradiated with benzene in ratios varying from 19:1 to 1:19 in the absence and presence of cyclohexane, diethyl ether, acetonitrile, or methanol and under air or argon atmospheres. Although in some cases minor amounts of reaction products were observed, from no experiment was there evidence for the formation of 1:1 adducts.

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