

The Photoaddition of Ethylenic Hydrocarbons to Benzene

By Derek Bryce-Smith,* Brian Foulger, John Forrester, Andrew Gilbert,* Brian H. Orger, and Hilary M. Tyrrell, Chemistry Department, University of Reading, Whiteknights, Reading, Berkshire RG6 2AD

The photoreactions of a range of acyclic and cyclic ethylenic hydrocarbons with benzene are described. The processes which occur depend on the ethylene, and in particular on its ionisation potential relative to that of benzene, but in general, *meta*-cycloadditions occur in every case and often predominate. *ortho*-Cycloaddition tends mostly to occur with the ethylenes of lowest ionisation potential relative to that of benzene, and *para*-cycloaddition occurs with cyclobutene to a significant extent, but not with cyclopropene or cyclopentene. Acyclic ethylenes containing the group $\text{Me}_2\text{C}=\text{C}$ also undergo ene-type acyclic *para*-addition to benzene to give cyclohexa-1,4-dienes.

The *ortho*-, *meta*-, and *para*-cycloadditions are stereospecific with respect to the ethylene, but the ene-addition is non-stereospecific. The former are mostly insensitive to solvent polarity, the exception being *ortho*-cycloaddition of 2,3-dimethylbut-2-ene which is definitely promoted by polar solvents. The ene-addition of 2,3-dimethylbut-2-ene was promoted by methanol but not by acetonitrile: the use of CH_3OD led non-stereospecifically to incorporation of deuterium in the 4-position of the adduct.

Cyclohexene was anomalous in giving mainly a mixture of three cyclobutane dimers, with only minor proportions of the *endo* and *exo,meta*-adducts and possibly a trace of the *para*-cycloadduct. The photocyclisation of benzene to give a range of essentially saturated polymers up to ca. $(\text{C}_6\text{H}_6)_{24}$ can be initiated by traces of *cis*-cyclo-octene.

All the products, with the exception of the cyclobutane dimers from cyclohexene, are considered to be formed *via* S_1 benzene, although T_1 benzene-sensitised *cis-trans* isomerisation of the ethylenes also slowly occurs: thus prolonged irradiation of *cis*-cyclo-octene and benzene leads eventually to the formation of *trans*-cyclo-octene and the corresponding cycloadducts.

The mechanisms of these processes are discussed with reference to orbital symmetry considerations, and the observed effects of polar solvents and proton donors. Only the *meta*-cycloadditions appear to occur by concerted processes involving either initial *meta*-bonding in S_1 benzene or initial *meta*-cycloaddition of the ethylene to S_1 benzene. The *ortho*- and *para*-cycloadditions are formally forbidden as concerted processes from S_1 benzene plus S_0 ethylene, and these are considered to involve intermediates having a degree of dipolar character.

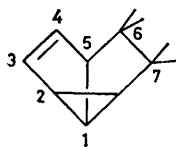
FOLLOWING the discovery in 1959 that maleic anhydride forms a remarkably stable 2 : 1 photoadduct with benzene,¹ numerous other examples of photochemical cycloaddition of ethylenic compounds to the benzene ring have been reported.² Examples of *ortho*-, *meta*-, and *para*-cycloadditions of ethylenes to benzene, and also ene-addition, are now known.²⁻⁷ The *meta*- (or

of previous reports and preliminary communications.^{7,10} As will be noted, the major reaction mode is *meta*-cycloaddition, but other processes frequently occur, and can even predominate.† No two systems have given identical results, and cyclohexene falls particularly out of line, as will be seen below.

RESULTS

Details of the irradiation conditions are described in the Experimental section. No significant effect of air or nitrogen atmosphere was observed, and although the use of low- or medium-pressure mercury-arc lamps gave broadly similar results, the former were preferred for their selective excitation and lower heating effect. Preparative experiments generally involved undiluted solutions of the addends, but in some systems the ratios and amounts of particular adducts were significantly dependent upon the proportions of the olefin and arene, the nature of the diluant, and the period of irradiation. In general all quantum-yield measurements were performed using iso-octane solutions 1.1M in benzene and 3.5M in the olefin at 20 °C, and using a low-pressure lamp. Most of the detailed work has been concerned with the photoadditions of *cis*- and *trans*-cyclo-octene to benzene.

Photoaddition of Cycloalkenes to Benzene.—(a) *cis*-Cyclo-octene. Our earlier observations with *cis*-cyclo-octene had shown that the predominant reaction mode with benzene was *meta*-cycloaddition, although products from other minor reactions were also detected.⁹ We now report that the 254-nm irradiation of a 1 : 3 v/v mixture of benzene and *cis*-cyclo-octene leads to three 1 : 1 adducts ($M = 188$): prolonged irradiation also yields a higher-boiling mixture which is comprised of at least four 2 : 1 benzene-cyclo-octene adducts, and traces (together <0.1%) of a 1 : 2 benzene-cyclo-octene adduct and cyclo-octylbenzene, the latter two being detected by high-resolution mass spectro-

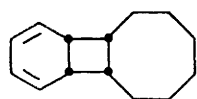


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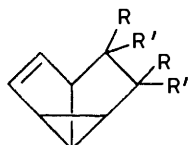
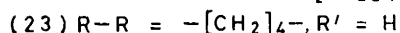
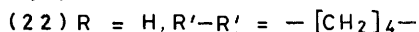
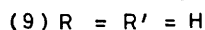
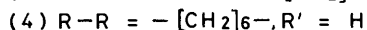
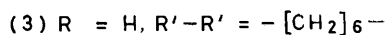
1,3-) cycloadditions of simple mono-ethylenic hydrocarbons to benzene are probably the most extraordinary, and were reported independently by two groups.^{8,9} They give products of type (1), sometimes in high chemical and quantum yields; but the factors which determine the relative tendencies for *ortho*-, *meta*-, and *para*-additions in particular cases have proved difficult to establish, and only now do we feel able to bring together the various preliminary reports^{3,7,9} in a coherent full form. In the present paper, we describe the photoreactions of benzene with the C_3 – C_9 cycloalkenes, 2-methylpropene, 2-methylbut-2-ene, 2,3-dimethylbut-2-ene, and *cis*-di-*t*-butylethylene, and we discuss the findings in relation to the ionisation potential differences and orbital-symmetry factors which have formed the subject

† The term *meta*-addition has previously been described in the literature as 1,3-addition, but is now preferred as a generic term since it avoids the ambiguities which otherwise arise with additions to substituted benzenes.¹¹

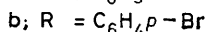
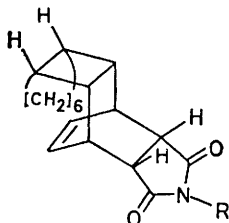
metry.¹² The 1:1 adducts were formed in the initial ratios 1:0.8:3.4, and showed respective relative retention times on Carbowax 20M of 0.85, 0.95, and 1.00. They are respectively assigned the *endo-ortho*-structure (2), the *exo-meta*-structure (3), and the *endo-meta*-structure (4), on the basis of the following evidence.



(2)



The adduct (2) of shortest retention time was both thermally and photochemically labile, fragmenting readily in the mass spectrometer to starting materials, and was efficiently removed from the other 1:1 adducts by maleic anhydride and other common dienophiles. All these properties are consistent with the *ortho*-adduct structure (2). Because of the photolability of this adduct, only very minor amounts could be prepared using short irradiation periods and low-intensity lamps. It was observed that the two 1:1 adducts of longer retention time could be almost completely removed by shaking the adduct mixture with methanolic mercuric acetate.¹³ The residual oil had predominant resonances in the n.m.r. spectrum at δ 5.50, 3.18, and 2.1—1.0: the first two resonance positions are in good agreement with those of the vinylic and allylic protons, respectively, in other bicyclo[4.2.0]octa-2,4-diene systems. The proton integrals were, however, unsatisfactory and the chromatogram of the sample indicated the presence of adducts having much longer retention times. Other chromatographic attempts to purify the minor adduct (2) were unsuccessful, but it was obtained as its Diels-Alder adducts with *N*-phenylmaleimide (m.p. 226—228 °C), *N*-(*p*-bromophenyl)maleimide (m.p. 253 °C), and maleimide (m.p. 309—310 °C). The elemental analyses and spectroscopic properties of these 1:1:1 adducts were all consistent with the assigned structures (5a—c). Further, an *X*-ray



study of the maleimide adduct (5c) clearly showed that the benzene and *cis*-cyclo-octene moieties had an *endo* configuration in the 1:1:1 adducts, from which it reasonably follows that the original 1:1 *ortho*-photoadduct has the *endo* structure (2).¹⁴ The conclusion that only one *ortho*-

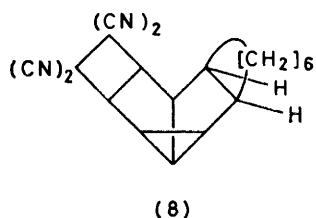
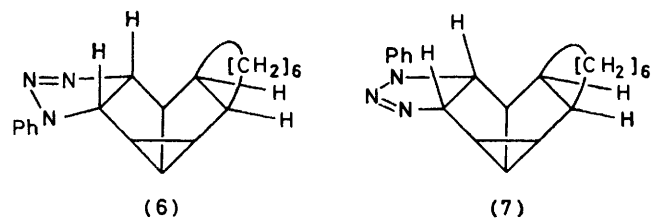
adduct had been formed is based on the fact that no other 1:1 adducts were detected under a wide variety of chromatographic conditions, and that the *ortho*-adduct reacted quantitatively with dienophiles to yield 1:1:1 adducts of sharp melting points and completely reproducible spectra, both of which are inconsistent with a mixture of isomers. If the isomeric *exo-ortho*-adduct had been formed, these results indicate that it would have had to be much more thermally and/or photochemically labile than the *endo* isomer. But consideration of the structures suggests no grounds for expecting this; indeed, greater repulsive interactions might well render the *endo* isomer (2) the less stable. We conclude that the *ortho*-cycloaddition occurs with high *endo* stereoselectivity.

Since the adduct (2) was very photolabile, the other two adducts (3) and (4) could be readily obtained essentially free from this isomer by prolonged irradiation followed by simple vacuum distillation (b.p. 80—82 °C at 0.2 mmHg). Using a 'scraper cell' apparatus designed to prevent occlusion of the fused quartz transmitting surfaces by polymeric by-products,¹⁵ and two 500-W medium-pressure mercury lamps, yields of these two adducts of approximately 2 g h⁻¹ have been recorded over periods of ≥ 15 h. Pyrolysis of this mixture of adducts (3) and (4) (ratio approximately 5:18 from preparative experiments) at 350 °C under nitrogen gave no detectable traces of benzene, but at temperatures above 200 °C the minor component (3) was quantitatively converted into an isomer of retention time 0.62 relative to the major 1:1 adduct (4). The major 1:1 benzene-*cis*-cyclo-octene adduct was isolated essentially pure by preparative g.l.c., and a 60% enriched sample of the minor isomer was obtained by column chromatography (silica gel). The ultraviolet spectrum of the major isomer had λ_{max} 219 nm (ϵ 2 850 l mol⁻¹ cm⁻¹) consistent with the vinylcyclopropane chromophore.

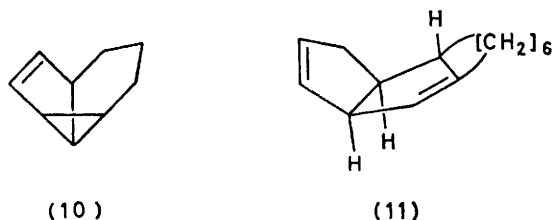
The i.r. spectrum had at least three unresolved bands between 3 000 and 3 050 cm⁻¹, the region characteristic of vinyl and cyclopropyl C-H stretching modes. The benzene origin of these absorptions was confirmed by their absence in the corresponding spectrum of the adduct from hexadentriobenzene and *cis*-cyclo-octene, and the appearance of three bands in the C-D stretching region between 2 100 and 2 300 cm⁻¹. Conclusive assignment of the *meta*-adduct structure to the major photoproduct of benzene and *cis*-cyclo-octene was provided by its n.m.r. spectrum (100-MHz in CCl₄) which is given, together with the assignments, in the Experimental section. In agreement with structure (4), the major 1:1 adduct readily added 1 mol of phenyl azide in refluxing benzene to give the triazoline (6), m.p. 162—164 °C, which lost nitrogen at approximately 160 °C, or photolytically, presumably to give the aziridine. The alternative triazoline structure (7) is rejected on the basis of the molecular dimensions of the unit cell (3 × 5 × 5.5 Å),¹⁶ and from the consideration that the aryl nitrogen would preferentially be attached to the carbon atom adjacent to an electron-rich centre, the cyclopropyl ring. This benzene-*cis*-cyclo-octene adduct also reacted slowly with tetracyanoethylene in benzene to yield a saturated compound (m.p. 213—214 °C) which had elemental analysis and spectroscopic properties consistent with structure (8).

The mixture enriched 60% in the minor 1:1 isomer had spectroscopic properties which, when corrected for the presence of the major adduct, were very similar to those of the major 1:1 adduct. Thus the n.v. spectrum had λ_{max} 208 nm (ϵ 3 200 l mol⁻¹ cm⁻¹) and only minor differences

were observed in the two i.r. spectra. The presence of the same ring systems in the major and minor 1:1 adducts is strongly indicated by the close similarity of the n.m.r. spectra and suggests that the major and minor adducts are in fact *endo* and *exo* stereoisomers, respectively, of the *meta*-structure (1). It is well known that vinylcyclopropane



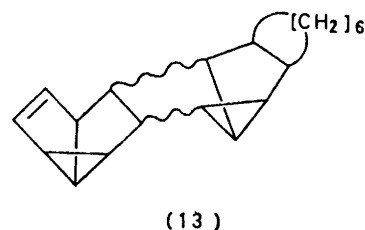
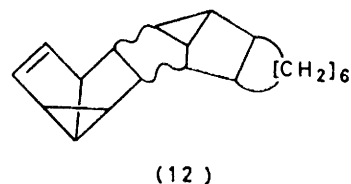
systems such as (9) and (10) thermally isomerise *via* a suprafacial 1,5-sigmatropic hydrogen shift.¹⁷ This type of rearrangement will only readily occur for the *exo* isomer (3) which has the required *endo* hydrogen at C-7. Hence the thermally labile minor *meta*-adduct is assigned structure (3), and the more stable major adduct structure (4). In agreement with these assignments, the thermally isomerised product (200 °C for 1 h under N₂) from the minor *meta*-adduct (3) has been deduced to have structure (11) from its



spectroscopic properties, its consumption of 2 mol of hydrogen on catalytic hydrogenation, and the absence of a *cisoid* 1,3-diene structure as inferred from its unreactivity towards common dienophiles. The major 1:1 *meta*-adduct (4) proved to be remarkably thermally stable: its vinylcyclopropane-cyclopentene rearrangement would be degenerate. This differing thermal lability of benzene-olefin *meta*-cycloadducts provides a convenient method for assessing the relative amounts of the *exo* and *endo* stereoisomers.¹⁸

The higher-boiling (140–145 °C at 0.5 mmHg) fraction from the irradiation of benzene and *cis*-cyclo-octene was not completely resolved by gas-liquid chromatography (silicone gum rubber SE30), but at least four major components were detected in an approximate ratio of 6:3:2:1. Elemental and mass spectrometric analysis of the mixture showed that it was comprised of 2:1 benzene-cyclo-octene adducts. Very minor amounts (together <0.1%) of an unidentified 1:2 benzene-cyclo-octene adduct and cyclo-octylbenzene were also detected in this mixture by mass spectrometry.¹² The 60 MHz n.m.r. spectrum of the

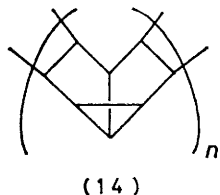
mixture in CCl₄ was consistent with mono-olefinic 2:1 benzene-olefin adducts as the ratio of vinyl:saturated proton resonances was 2:24. The i.r. spectrum of the mixture was very similar to those of the 1:1 *meta*-adducts above 1300 cm⁻¹: the characteristic C=C band at 1600 cm⁻¹ suggests the presence of a small-ring olefin. Above 3000 cm⁻¹, the strong absorption attributed to =CH and cyclopropyl C-H stretching vibrations in the 1:1 *meta*-adducts was again present, but the band at 3010 cm⁻¹ was increased in intensity relative to the band at 3040 cm⁻¹ when compared with the 1:1 adducts, implying a change in the ratio of cyclopropyl to vinyl C-H bonds. The u.v. spectrum of the 2:1 adduct mixture (hexane) had a shoulder at 220 nm and no maximum above 200 nm. Structures (12) and (13) for the 2:1 adducts are consistent with the above spectroscopic data. Thus these 2:1 adducts evidently arise from a second *meta*-addition of benzene to the 1:1 *meta*-adducts (3) and (4). In other words, the first-formed *meta*-1:1 adducts (3) and (4) can function as the olefinic partners in further olefin-benzene cycloadditions.



(b) *Photopolymerisation of benzene initiated by cis-cyclo-octene.* In agreement with the foregoing results, the formation of the 2:1 adducts was found to be very dependent upon both the ratio of benzene and cyclo-octene in the original mixture, and the irradiation time. Thus a low concentration (*ca.* 10%) of *cis*-cyclo-octene in benzene and prolonged irradiation increased the proportion of the 2:1 adduct mixture. The initial addition of benzene to the olefin may thus be considered as the first step in the photopolymerisation (more strictly phototelomerisation) of benzene. Indeed, when benzene is irradiated with 0.35 mol % of cyclo-octene or 0.06 mol % of the 1:1 *meta*-adduct mixture [(3) + (4)], products of molecular weights ranging from *ca.* 750 to 2000 are obtained.¹⁹ These correspond to the subsequent addition of 8–24 benzene units to the 1:1 adduct. The properties of these 'polybenzenes', in particular the non-aromaticity and substantial absence of ethylenic unsaturation (n.m.r. spectra) suggest that, apart from the end groups, their structures are based on the repeating C₆H₆ unit (14).

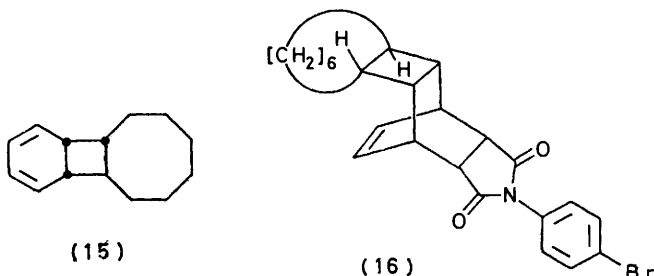
(c) *trans-Cyclo-octene.* Irradiation of benzene in the presence of decreasing amounts of *cis*-cyclo-octene yielded increasing amounts of 1:1 cycloadducts other than those described above: these new adducts were subsequently shown to be derived from *ortho*- and *meta*-cycloadditions of benzene to *trans*-cyclo-octene. This latter was detected in

the irradiated solution and doubtless arose by triplet benzene-sensitised isomerisation of the *cis*-olefin, a process for which there are many precedents.²⁰ Formation of triplet benzene would be expected to be favoured at the



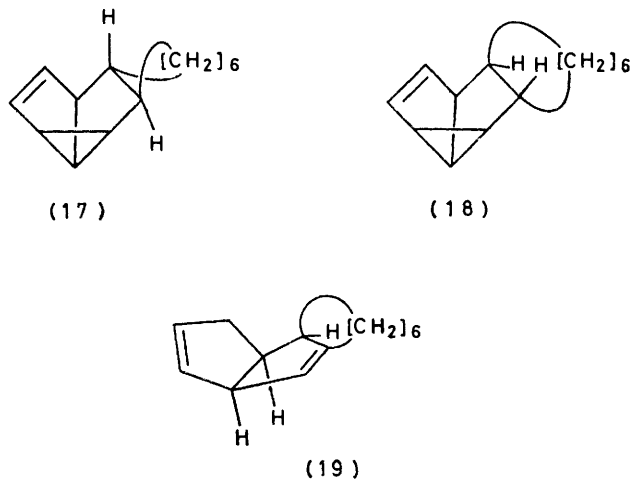
higher benzene concentrations as these would favour the formation of the benzene excimer, a species known to dissociate to triplet benzene.²¹

In a separate experiment, irradiation of benzene and *trans*-cyclo-octene yielded three 1:1 adducts ($M = 188$) in the *initial* ratios 1:2.6:1 in order of increasing retention time on Carbowax 20 M. The major component of the mixture, unlike the two minor products, fragmented readily in the mass spectrometer to starting materials, was removed from the mixture by maleic anhydride and other common dienophiles, and was destroyed by irradiation of its solution through a Pyrex filter or on heating the mixture in the g.l.c. injection block at temperatures $>350^\circ\text{C}$; these properties are consistent with the *ortho*-cycloadduct structure (15) for the major product. In view of the lability of this product it was isolated as its Diels-Alder adduct with *p*-bromo-*N*-phenylmaleimide, m.p. $273\text{--}274^\circ\text{C}$. The n.m.r. spectroscopic data for the 1:1:1 adduct (see Experimental section) are consistent with structure (16) and are very similar to those of the previously mentioned maleimide-benzene-*cis*-cyclo-octene adduct (5b) with the notable exception that in adduct (16) the vinyl protons resonate as a double doublet ($J_{\text{vic}} 10\text{ Hz}$, $J_{\text{allylic}} 2\text{ Hz}$) whereas in the latter this resonance appears as a triplet: this feature is consistent with the two non-equivalent vinyl protons in adduct (16).²²



As a result of the photolability of the *ortho*-cycloadduct (15), prolonged irradiation of *trans*-cyclo-octene and benzene yielded essentially a 1:1 mixture of the two 1:1 adducts which had appeared as minor products on brief irradiation. The i.r. and n.m.r. spectra of the mixture were very similar to those of the *meta*-cycloadducts (3) and (4) of *cis*-cyclo-octene and benzene, but with the noteworthy exception that in the adducts (3) and (4) the methylene scissoring vibration at *ca.* 1460 cm^{-1} was resolved into two distinct bands ($\Delta\nu 20\text{ cm}^{-1}$). This is taken as evidence for the *cis*-fusion of the cyclo-octane ring, for this band appears virtually as a singlet in the i.r. spectra of the *trans*-cyclo-octene adducts, consistent with *trans*-fusion of the cyclo-octane ring. From the spectroscopic data of the mixture, the two initially minor products from *trans*-cyclo-octene

and benzene are assigned the *meta*-adduct structures (17) and (18). Of these adducts, that of longer g.l.c. retention time on Carbowax 20M was isomerised at 200°C to yield (19) by a 1,5-sigmatropic shift similar to that involved in the rearrangement of (3) to (11), and is thus assigned structure (18) which has the necessary *endo* C-7 hydrogen. The other isomer must, therefore, have the remaining *trans*-*meta*-structure (17) and at 300°C , this isomer also gave (19). This behaviour is rationalised by a vinylcyclopropane-cyclopentene rearrangement of (17) at the higher temperature which effectively yields the isomer (18); but under the conditions of the experiment this latter is readily converted into (19). It is interesting to recall here that the analogous



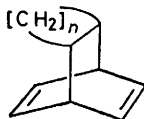
rearrangement of isomer (4) would be degenerate, as previously noted, and would not provide the corresponding isomer bearing a C-7 *endo* hydrogen, and hence would not render possible the 1,5-sigmatropic shift to give (11). Indeed compound (4) proved to be remarkably stable and brief heating at 450°C produced little change, other than tar formation, detectable by g.l.c.

(d) *Cyclopentene, cycloheptene, and cis-cyclononene*. Irradiation of solutions of cyclopentene, cycloheptene, and *cis*-cyclononene in benzene at 254 nm gave *meta*-cycloadducts as the major products in each case. The structures were assigned from spectroscopic properties, and the relative proportions of *exo* and *endo* isomers were deduced from the greater thermal lability of the *exo* isomers, as with the corresponding adducts from *cis*-cyclo-octene.¹⁸ Data for the cycloalkenes are given in the Table.

Minor amounts of cyclobutane dimers ($\Phi = 0.06$) were produced from cyclopentene together with a trace of a further 1:1 adduct with benzene. This latter product underwent ready pyrolysis to the starting materials at $>200^\circ\text{C}$, and similarly fragmented in the mass spectrometer. The amounts formed of this product precluded its isolation and structural determination, but the above properties, coupled with its insensitivity to dienophiles, suggest the 1,4-cycloadduct structure (20) for this compound.

Cycloheptene and benzene gave the expected *endo* and *exo meta*-cycloadducts, and minor amounts of four other products. One of these additional products was only formed during prolonged irradiation with a medium-pressure lamp and had a parent ion consistent with a dimer of cycloheptene. Because of their low concentrations it proved impractical to identify the other minor products.

cis-Cyclononene and benzene gave the *endo* and *exo meta*-cycloadducts, and also minor amounts of other 1 : 1 adducts. The photolabilities and mass-spectral fragmentation of the minor reaction components indicated that none was an



$$(20) n = 3$$

$$(21) n = 4$$

$$(30) n = 2$$

$$(32) n = 1$$

ortho-cycloadduct, but the amounts formed were again too small for other structural studies.

approximately 90% of the product mixture. This effect is readily attributable to the previously noted phenomenon whereby increased concentrations of benzene promote formation of the benzene excimer and thence by dissociation of this, triplet benzene²¹ which then sensitises the ethylene dimerisation. We shall return later to the intriguing question whether triplet cyclohexene or highly strained *trans*-cyclohexene is the immediate precursor of the three dimers.

Of the mixture of 1 : 1 cyclohexene-benzene adducts, only three components could be resolved by analytical g.l.c., and then only partially so; but there was evidence for the presence of at least two further adducts in the mixture. These difficulties, coupled with the very small amounts of products formed, rendered it impractical to isolate the individual components. The three 1 : 1 adducts were formed in the appropriate ratios 1.0 : 1.8 : 0.6 in order of

TABLE

Olefin	Ionisation potential (eV)	Δ I.P. of benzene and alkene	Type of adduct with benzene (Φ)	Other products
2,3-Dimethylbut-2-ene	8.3 ^a	0.94	<i>ortho</i> (0.25), <i>meta</i> (0.03), 'ene' (0.03)	
<i>trans</i> -Cyclo-octene	8.51 ^a	0.83	<i>ortho</i> (0.37), <i>meta</i> (0.14, 0.14)	
2-Methylbut-2-ene	8.67 ^b	0.57	<i>ortho</i> (0.05), four <i>meta</i> (0.18 total), two 'ene' (0.07 total)	
<i>cis</i> -Di- <i>t</i> -butylethylene	8.71 ^a	0.53	No products observed, slow formation of the <i>trans</i> isomer on prolonged irradiation	
<i>cis</i> -Cyclo-octene	8.75 ^a	0.49	<i>ortho</i> (0.09), <i>endo meta</i> (0.31), <i>exo meta</i> (0.07)	
<i>cis</i> -Cyclononene	8.78 ^a	0.46	<i>endo meta</i> (0.13), <i>exo meta</i> (0.02), two further 1 : 1 adducts ($M^+ = 202$) of unknown structure (0.02)	
Cycloheptene	8.86 ^a	0.38	<i>endo meta</i> (0.16), <i>exo meta</i> (0.11)	Minor amounts of other products one of which appears to be an alkene dimer
Cyclohexene	8.94 ^b (9.12) ^c	0.3 (0.12)	Low yields of three 1 : 1 adducts: tentative assignment as <i>exo meta</i> , <i>endo meta</i> , and <i>para</i> in approximate ratio 1.0 : 1.8 : 0.6	Low yields of three alkene dimers
Cyclopentene	9.02 ^a (9.18) ^c	0.22 (0.06)	<i>endo meta</i> (0.17), <i>exo meta</i> (0.02), trace of further adduct: tentative assignment <i>para</i>	Minor amounts of alkene dimers
Isobutene	9.23 ^{b d}	0.01	Two regio-isomers of <i>meta</i> , 'ene' product, ratio ca. 9 : 1	
Cyclobutene	9.43 ^c	0.19	<i>endo meta</i> , <i>para</i> ratio 9 : 1 (cf. ref. 39)	
Cyclopropene	9.86 ^c	0.62	Three 1 : 1 adducts, tentatively assigned as arising from <i>meta</i> cycloaddition and at least four 2 : 1 alkene-benzene adducts	

^a Measured on a Perkin Elmer PS-18 Photoelectron Spectrometer. ^b K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectroscopy Radiative Transfer*, 1962, **2**, 369. ^c P. Asmus and M. Klessinger, *Tetrahedron*, 1974, **30**, 2477. ^d R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.*, 1960, **A258**, 459.

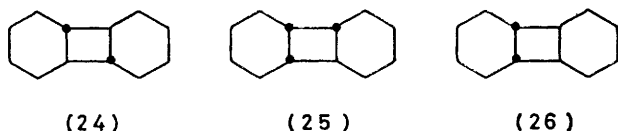
(e) *Cyclohexene*. Irradiation of mixtures of benzene and cyclohexene yielded results quite different from those described above for other cycloalkenes: the major products were cyclohexene dimers. It is already known that simple benzenoid compounds can sensitise the photodimerisation of cyclohexene.²³ Irradiation of a 10% v/v solution of benzene in cyclohexene at 254 nm led to the slow formation of at least eight volatile products. By mass-spectrometry-g.l.c., the components of the mixture were shown to consist of two groups of products. The three of shortest retention times were dimers of cyclohexane, and constituted approximately 30% of the mixture. The remainder were all 1 : 1 adducts of benzene and cyclohexene.* The proportions of adducts and dimers from benzene and cyclohexene were very dependent upon the reactant concentrations; but at a cyclohexene : benzene ratio of 1 : 9, the dimers constituted

increasing retention time on a Carbowax 20M column. The product of longest retention time fragmented readily to starting materials in the mass spectrometer, so was probably an *ortho*- or *para*-cycloadduct, whereas the other two products had prominent M^+ ions suggestive of *meta*-cycloadducts. The action of heat on the mixture of 1 : 1 adducts was interesting. The component of shortest retention time isomerised essentially quantitatively at ca. 300 °C, whereas the major adduct appeared to be remarkably thermally stable. The adduct of longest retention time disappeared from the chromatogram at a temperature of 400 °C without the concomitant production of isomers: this behaviour would be consistent with thermal dissociation of an *ortho*- or a *para*-adduct to the starting materials. But none of the components of the 1 : 1 adduct mixture was reactive towards maleic anhydride and other common dienophiles, so the presence of *ortho*-adducts may be discounted with some confidence. From these observations we tentatively conclude that the three 1 : 1 adducts of

* Ethylene dimers and 1 : 1 cycloadducts are also formed from the irradiation of benzene in the presence of norbornene²⁴ and cyclohexa-1,4-diene.²⁵

cyclohexene and benzene resolved by analytical g.l.c. are, in respective order of increasing abundance, the *para*-cycloadduct (21) and the *exo* and *endo meta*-cycloadducts (22) and (23).

We now return to a consideration of the cyclohexene dimers. As mentioned above, irradiation of a benzene-cyclohexene (9 : 1) mixture yielded the three olefin dimers almost free of 1 : 1 adducts. The relative proportions of the three dimers to each other were dependent upon the concentrations of benzene and cyclohexene. Thus whereas the product of shortest retention time on Carbowax 20M always constituted *ca.* 25% of the dimer mixture, the ratio of the other two dimers varied between approximately 1 : 2 and 2 : 1 for corresponding 1 : 9 and 9 : 1 ratios of benzene and cyclohexene respectively. The n.m.r. spectrum of a distilled sample of the dimer mixture showed no resonances at lower field than δ 2.3, and two complex resonances in the region δ 1.6—1.0 region. Thus, ethylenic protons are absent, so the three dimers must be stereoisomers of the basic ($2\pi + 2\pi$) cyclobutane structure. We have assigned structures (24), (25), and (26) to these photo-



dimers of cyclohexene (in order of increasing retention time) by comparison of the g.l.c. properties with those of dimers of established structure prepared by the methyl acetoacetate-sensitised dimerisation of cyclohexene.²⁶ No dimerisation was detected on irradiation of cyclohexene in the absence of benzene, so energy transfer from triplet excited benzene is evidently essential, as earlier reported by Kropp.^{23,27} Triplet cyclohexene is thus initially produced but this might in principle transform into the highly-strained *trans*-isomer, which itself might cycloadd thermally to cyclohexene by an *sa* process. The formation of *three* cyclobutane dimers tends to argue against the direct involvement of *trans*-cyclohexene, since this would be expected to yield a single dimer, whereas triplet cyclohexene would be more likely to add non-selectively.

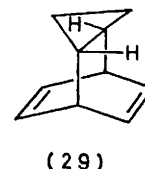
We have, however, attempted to determine whether *trans*-cyclohexene could be detected as an intermediate. Low temperature (-70 °C) irradiation of mixtures of benzene and cyclohexene at 254 nm in a methylcyclohexane-propan-2-ol glass revealed no sign of i.r. absorption bands attributable to a *trans*-alkene (970 — 960 cm^{-1}), yet significant amounts of dimers were formed. This result suggested that any *trans*-cyclohexene formed is extremely labile even at -70 °C, whether or not it is involved in the dimerisation process. However, attempts to trap the intermediate in the dimerisation reaction were partly successful. Thus irradiation of benzene and cyclohexene in the presence of furan (ratio 9 : 1 : 1) led to a dramatic decrease in the formation of dimers (now 15% of all photoproducts) and the production of apparently two 1 : 1 adducts ($M^+ = 150$) of cyclohexene and furan which constituted 6 and 60% of all photoproducts. These new products were not formed on irradiation of cyclohexene and furan in the absence of benzene, so probably arise *via* triplet benzene sensitisation. But the presence of furan did not appreciably affect the formation of benzene-cyclohexene adducts under these conditions, although minor amounts of benzene-furan photoadducts were detected.²⁸ It proved feasible to isolate by preparative

g.l.c. only the major cyclohexene-furan adduct, but the use of silver nitrate-impregnated silica t.l.c. plates resolved this product into a major and minor isomer: again only the major isomer was isolated. (Thus there were at least three cyclohexene-furan adducts in all). The mass spectrum of the isolated adduct had a low-abundance parent ion but its fragmentation into starting materials was facile, and indicated that both the furan and cyclohexene rings were intact. The n.m.r. spectrum of the compound consisted of essentially six resonances in the ratio 1 : 1 : 1 : 1 : 2 : 8 (increasing field) and is detailed in the Experimental section. The inter-relationship of the five lower-field resonances was demonstrated by decoupling experiments



and indicated that only one compound was present. The assignment of structure (27) to the cyclohexene-furan adduct was made essentially from the n.m.r. spectrum and its comparison with those of 2,3- and 2,5-dihydrofuran derivatives. We have been unable to prove conclusively that (27) was a *primary* photochemical product, but the possibility of its formation by thermal rearrangement during isolation and purification was eliminated. No evidence was obtained for the formation of (28), the Diels-Alder cycloadduct of *trans*-cyclohexene and furan; and the absence of this, in conjunction with the presence of at least three cyclohexene-furan adducts, argues against any unique intermediacy of the *trans*-ethylene, and in favour of a direct reaction between T_1 and S_0 cyclohexene as the source of the dimers. The absence of an allylic-isomer of (27) suggests that a free-radical mechanism was not involved.

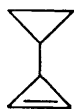
(f) *Cyclobutene*. In agreement with Srinivasan,²⁹ we have found that cyclobutene gives both *meta*- and *para*-cycloadducts with benzene: the former mode of reaction predominates and the major *meta*-isomer has *endo* stereochemistry. It was of particular interest to determine the stereochemistry of the *para*-adduct since orbital symmetry considerations suggest that concerted *cis-para*-cycloaddition of S_0 ethylene to benzene should be forbidden for the S_1 arene, but allowed from the T_1 arene, whereas a corresponding *trans* process leading to the more strained adduct (29) should be allowed. The *para*-cycloadduct is thermally converted into starting materials at temperatures of 200 °C, and readily decomposes in the mass spectrometer to starting materials. The n.m.r. spectrum of the *para*-cycloadduct is consistent with the *cis*-adduct structure (30): in parti-



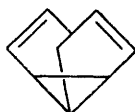
cular, the vinyl proton resonances appear as two sets of doublets rather than one. To confirm the *cis* assignment and to investigate whether minor amounts of the *trans* adduct were also present, the *para*-cycloadduct was oxidised to cyclobutane-1,2-dicarboxylic acid and esterified with diazomethane. The g.l.c. properties of the

diester were compared with those of authentic dimethyl *cis*- and *trans*-cyclobutane-1,2-dicarboxylate.³⁰ Only the *cis* dimethyl ester ($\geq 99.5\%$) was detected in the esterified oxidised *para*-cycloadduct. This observation is in principle contrary to the orbital symmetry prediction for a singlet process, and suggests either a triplet process and/or that the addition is non-concerted, or that adduct (29) rapidly isomerises into (30).

(g) *Cyclopropene*. Irradiation of an approximately 5% v/v solution of cyclopropene in benzene led to the formation of minor amounts of three 1:1 adducts, the proportions of which were time-variant and which also changed on storage at -10°C in the dark, the proportion of one of the products increasing at the expense of another. At least four 2:1 cyclopropene-benzene adducts were also formed. It has been reported that cyclopropene undergoes thermal dimerisation to the highly reactive ethylene (31) in dilute solutions

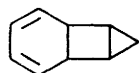


(31)

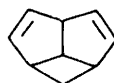


(33)

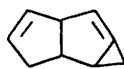
at -25°C ³¹ and thus the apparent 2:1 addition could in principle result from 1:1 addition of the dimer (31) to benzene and/or from secondary reaction of cyclopropene with 1:1 adducts. The 1:1 adducts all had similar mass-spectral breakdown patterns with base peaks at m/e 117 ($M-1$) and major ions at 118 (M^+), 115, and 91. The *para*-cycloadduct (32) was synthesised from maleic anhydride and cycloheptatriene followed by electrochemical decarboxylation, but was shown by g.l.c. to be absent from the irradiated solution, as were allylbenzene and cyclopropylbenzene. Compound (32) is, however, reported to be photolabile and to yield (33) upon irradiation in pentane-acetone solution.³² Irradiation of (32) as a 2% solution in benzene in the present study produced a rapid isomerisation to one major product which was absent from the mixture of benzene-cyclopropene photoadducts. Evidently *para*-cycloaddition of cyclopropene to benzene did not occur to any appreciable extent (contrast cyclobutene). None of the 1:1 adducts appeared to react with common dienophiles, so *ortho*-adducts (34) and 8,9-dihydroindene, produced *via* ring-opening of (34) and cyclisation of the resulting cyclononatetraene ($t_{1/2} = 14$ min at 40°C),³³ are evidently not among the three 1:1 adducts. Having eliminated the obvious substitution products and *ortho*- and *para*-cycloadducts and products derived therefrom, we therefore provisionally conclude that two of the three 1:1 adducts are the *exo* and *endo meta*-adducts and that the third is the rearranged product (35) derived from the *endo meta*-adduct



(34)



(35)

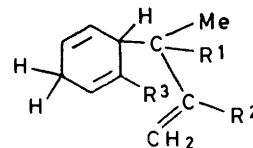


(36)

analogous to that formed from the corresponding cyclobutene adduct.³¹ Rearrangement by a 1,5-hydrogen shift is considered less probable since the product (36) would be in serious violation of Bredt's Rule. The very small amounts of products formed precluded their isolation, but all had significant molecular ions in their mass spectra consistent

with *meta*-cycloadducts, and fragmentation to starting materials appeared to be minimal.

Photoaddition of Acyclic Olefins to Benzene.—(a) 2,3-Dimethylbut-2-ene (Tetramethylethylene). For this alkene, we have reported in a preliminary communication that the *meta*-adduct is only a minor reaction product, the main product (37) being formed by a non-concerted 'ene-type'



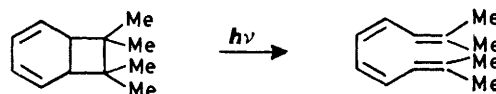
(37) $R^1 = R^2 = \text{Me}, R^3 = \text{H}$

(45) $R^1 = R^2 = R^3 = \text{Me}$

(47) $R^1 = \text{H}, R^2 = \text{Me}, R^3 = \text{H}$

(48) $R^1 = \text{Me}, R^2 = R^3 = \text{H}$

para-addition.³ In all, three 1:1 adducts ($M^+ = 162$) are formed. Their relative proportions were found to be dependent on both reactant concentration and irradiation time. Thus the photostationary concentration of the three adducts from irradiation of a 10% v/v solution of benzene in 2,3-dimethylbut-2-ene was approximately 1:4:4.5 in order of increasing retention time on Carbowax 20 M, whereas the use of a 10% solution of the alkene in benzene led to a photostationary ratio of *ca.* 1:4:8. Quantum-yield data for this system are given in the Table. It will be noted that the adduct of shortest retention time rapidly reaches a low photostationary concentration. It fragmented readily in the mass spectrometer, and underwent ready pyrolysis and photolysis to starting materials. Irradiation of its solutions also produced typical tetraene absorption bands at 288, 303, and 320 nm consistent with the process shown below. The assignment of structure (38) is

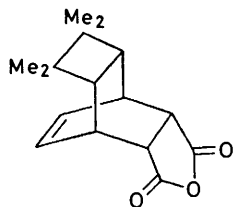


(38)

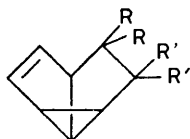
confirmed by the ready thermal addition of maleic anhydride to give the Diels-Alder adduct (39), m.p. 192–193 $^\circ\text{C}$, having the expected spectroscopic properties and elemental analysis (see Experimental section). The second most abundant adduct from the preparative experiment was obtained by preparative g.l.c. The spectroscopic data for this 1:1 adduct were in complete agreement with those reported earlier for the *meta*-cycloadduct (40).⁸

The major component (37) of the mixture from preparative experiments was obtained by g.l.c., although it always contained small but variable amounts of a 1:1 adduct minus 2 H. The dehydrogenated compound (41), together with other compounds of $M^+ = 166$ and 160, was readily formed on pyrolysis of the major *para*-ene-adduct (37); structural evidence for (37) and (41) is detailed in the Experimental section. This type of 'ene' product had not been reported from the irradiation of arene-alkene systems prior to the present work. The concerted process (42) was at first thought likely, but had to be rejected for the following reasons. Thermal dehydrogenation of the 'ene' product formed from C_6D_6 and 2,3-dimethylbut-2-ene

yielded the aromatic product by loss of both D₂ and HD. Since cyclohexa-1,4-dienes are known to undergo stereospecific *syn*-2,5-thermal elimination of hydrogen, this result indicates that the *syn*- and *anti*-adducts (43) and (44) are



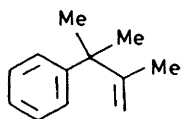
(39)



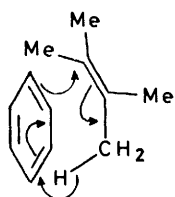
(40) R = R' = Me

(49) R = H, R' = Me

(50) R = Me, R' = H

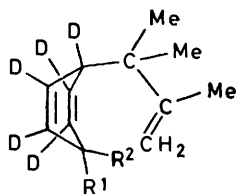


(41)



(42)

both produced in the photoreaction, and that the addition is therefore non-concerted. The ratio (43):(44) appears to be concentration dependent since the adducts formed from irradiation of a 10% v/v solution of the alkene in

(43) R¹ = D, R² = H(44) R¹ = H, R² = D

C₆D₆ underwent pyrolytic loss of D₂ and HD in the ratio of 2:7 respectively, whereas the corresponding ratio from the adducts produced from a 1% solution was 1:1. Evidently there was a greater contribution from intramolecular hydrogen-atom or proton transfer at the higher dilution within an intermediate diradical, exciplex, or zwitterion.

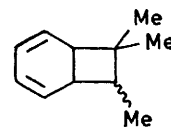
The question of whether the hydrogen is transferred as an atom or as a proton in the photo-'ene-reaction' was answered by a study of solvent effects. Irradiation of 2,3-dimethylbut-2-ene with benzene in cyclohexane, ether, methanol, and acetonitrile under comparable conditions gave the following results. The yield of the *meta*-cycloadduct was essentially the same in all four solvents, whereas that of the *ortho*-adduct was approximately 70–80% greater in both methanol and acetonitrile than in cyclohexane or ether. The yield of the 'ene' product was increased by ca. 35% in methanol, but the yield in acetonitrile was similar to that in the non-polar solvents. Further, irradiation of the alkene and benzene in the presence of MeOD led to 20% deuterium incorporation in the 4-position (based on CHD) of the cyclohexadiene moiety in (37), whereas no deuterium was incorporated in the dark or

on irradiation of pre-formed (37) in MeOD. Irradiation of MeOD in C₆H₆ led to no detectable incorporation of deuterium into the benzene. Thus proton-transfer is clearly involved in the formation of the 'ene' product, and the proton-transfer step evidently follows the initial addition of the alkene to the benzene ring. This result constitutes the first example of acid catalysis in a photoreaction between two hydrocarbons. The photoaddition reactions of 2,3-dimethylbut-2-ene to benzene were inhibited in the presence of the hydrogen-atom donor ethane-1,2-dithiol, a result consistent with the efficient interception of S₁ benzene by the thiol.

It is of interest to note here that the preparative irradiation of toluene and 2,3-dimethylbut-2-ene leads to four 1:1 adducts of the starting materials, of which one comprises approximately 65% of the mixture. This major adduct was separated by preparative g.l.c. and shown by spectroscopic analysis to be the 'ene' product (45) having the arene methyl group specifically located in the 2-position.

It was clearly of interest to compare the behaviour of 2,3-dimethylbut-2-ene with that of other methylated ethylenes. Several groups have already investigated the photoreactions of *cis*- and *trans*-but-2-ene with benzene.^{5,18,35}

(b) 2-Methylbut-2-ene (trimethylethylene). Irradiation of a 10% v/v solution of this alkene in benzene at 254 nm led to the formation of three products in the approximate ratio 14:1:5 in order of increasing retention time on Carbowax 20M. These ratios were time and atmosphere invariant, but a change of reactant proportions to 95% alkene and 5% benzene, and a short irradiation time (conditions conducive to the formation of *ortho*-cycloadducts⁵) allowed the detection of a new 1:1 adduct which rapidly reached a maximum of approximately 20% of the total adducts. But this proportion decreased on further irradiation, and the solution began to exhibit four absorption bands in the 280–330 nm region consistent with the formation of an octatetraene *via* secondary photolysis of a photolabile *ortho*-cycloadduct. Although the photolability of this 1:1 adduct prevented its formation in readily isolable amounts, its assignment as the *ortho*-cycloadduct (46) is supported by its ready fragmentation to starting materials in the mass spectrometer, and its removal from the mixture by treatment with maleic anhydride and other common dienophiles.

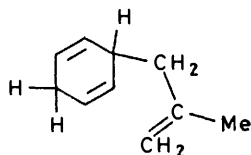


(46)

Two major groups of 1:1 adducts formed from prolonged irradiation of trimethylethylene and benzene were obtained as colourless oils by preparative g.l.c. The more abundant of these was shown by t.l.c. on silver nitrate-impregnated silica plates to be a mixture of four components, and to the eye the four t.l.c. spots were approximately equal in size and intensity. On the basis of the spectroscopic properties (see Experimental section), the four components are assigned the four possible isomeric *meta*-cycloadduct structures. In agreement with this assignment, heating the mixture at 250–300 °C caused approximately 25% of the product to be converted into an isomer which was isolated by preparative g.l.c., and shown by spectral analysis to be the

expected 3,4,4-trimethylbicyclo[3.3.0]octa-2,7-diene: the remaining mixture of three *meta*-cycloadducts was recovered unchanged. The other reaction component isolated from irradiation of trimethylethylene with benzene is assigned the 'ene' adduct structure (47), on the basis of its spectroscopic properties and comparison with those of (37). The 1:1 adduct formed in lowest yield is tentatively assigned the other possible 'ene' adduct structure (48) on the basis of its fragmentation pattern in the mass spectrometer. In particular the base peak corresponds to $C_6H_7^+$ and its formation is characteristic of acyclic *para*-benzene adducts such as the other 'ene' adduct described above, and those produced from aliphatic amines and benzene.³⁶

(c) *2-Methylpropene (isobutene)*. Irradiation of solutions of isobutene (approximately 5% v/v) in benzene led to the formation of three 1:1 adducts in the approximate ratios 5:4:1. The effects of change in reactant concentration, solvent, and irradiation time were not studied with this system, but following preparative experiments the irradiated solution showed typical 'tetraene' absorption in the 280–320 nm region, indicative of the prior formation of a photolabile *ortho*-cycloadduct. The three 1:1 adducts were isolated by preparative g.l.c., and by spectroscopic methods the two most abundant adducts (ratio 5:4) were assigned the *meta*-cycloadduct structures (49) and (50) respectively: these assignments were substantiated by pyrolysis experiments at 250–300 °C, when the more abundant adduct was essentially stable while the other was converted into an isomer identified as 4,4-dimethylbicyclo[3.3.0]octa-2,7-diene from its spectral characteristics. The minor adduct from this system was shown to be the 'ene' product (51).



(51)

The foregoing results for the addition of cyclic and acyclic ethylenes to benzene are summarised in the Table.

Solvent and Temperature Effects.—The formation of the *meta*-cycloadducts reported here was not influenced to any measurable extent by changes in solvent polarity or the presence of a proton donor such as methanol.* More powerful proton donors react non-photochemically with *meta*-cycloadducts.³⁹ As noted above, however, polar solvents promote the *ortho*-cycloaddition of 2,3-dimethylbut-2-ene to benzene, and a proton donor promotes formation of the 'ene' products. A change of temperature between 16 and 65 °C did not significantly affect any of the addition reactions reported here. With hexafluorobenzene, as we have previously reported, the *meta*-addition of cyclooctene is likewise insensitive to temperature changes, but *ortho*-addition was promoted by increasing the temperature of irradiation from 16 to 75 °C.⁴⁰

DISCUSSION

It is evident that the photoaddition of alkenes to benzene in the liquid phase is a very general process: and indeed the only mono-ene hydrocarbon which we have so far found not to photoadd is *cis*-di-*t*-butylethylene. The photoadditions fall into four categories: *viz.* *ortho*-, *meta*-,

and *para*-cycloaddition, and acyclic *para*-ene-addition. These are generally accompanied to a minor extent by benzene-sensitised *cis*-*trans* isomerisation of the alkene, even in the case of *cis*-di-*t*-butylethylene, which process is well-known, from previous physically-oriented studies, to involve principally energy transfer from T_1 benzene to produce T_1 alkene.⁴¹ On the other hand, the proposal by Bryce-Smith and Longuet-Higgins⁴² that the *meta*-cycloadditions should occur *via* S_1 benzene ($^1B_{2u}$) rather than triplet species has been supported by the work of Cvetanovich and his co-workers,³⁵ and Wilzbach and Kaplan have provided evidence that the *ortho*- and *para*-cycloadditions also proceed from S_1 benzene.⁵ This latter appears contrary to the original proposal in ref. 42 that triplet benzene should be involved, since it has the $^3B_{1u}$ symmetry required for concerted *ortho*- and *para*-cycloadditions; but it was subsequently shown¹⁰ that charge-transfer processes would also overcome the symmetry restriction. We further discuss the charge-transfer mechanism below, in connection with the dependence on ionisation-potential differences which has now been demonstrated.

The *para*-ene-additions also probably involve S_1 benzene since the ratios of 'ene'-adducts to the concurrently formed *meta*-cycloadducts are insensitive to major changes in the proportions of the reactants, which would have been expected to alter the ratios of T_1 to S_1 benzene. Although mono-alkenes are only rather weak quenchers of benzene fluorescence,⁴³ and although xenon exhibits an inhibitory effect on the gas-phase photoaddition of *trans*-but-2-ene to benzene which is more modest than might perhaps have been expected,³⁵ the balance of evidence suggests that all the photoadditions are singlet processes.

The Table summarises the results obtained for the photoaddition of a series of cyclic and acyclic alkenes to benzene. The experimental conditions were similar for each case (see Experimental section), except that the C_3 and C_4 alkenes, being gaseous, had to be used at lower concentrations than those employed for the other alkenes.

It will be seen that the reaction pathways followed depend considerably on the alkene involved: even in the series of C_3 – C_9 cycloalkenes no regular trend in behaviour with ring size is apparent. On the other hand, it is evident that *meta* addition tends to occur to the proportionally greatest extent when the difference between the ionisation potentials of the alkene and benzene is smallest. In the cases where $\Delta I.P.$ is $< ca. 0.6$, *meta*-cycloaddition predominates. When we first drew attention to a connection between $\Delta I.P.$ and the relative quantum yields for *meta*- and *ortho*-cycloaddition of an alkene to benzene,⁷ we noted that over the range of alkenes and substituted alkenes studied, $\Phi_{1,2} < \Phi_{1,3}$ when the ionisation potential of the alkene lies between 8.65 and 9.6 eV (I.P. benzene = 9.24 eV). Thus *ortho*-

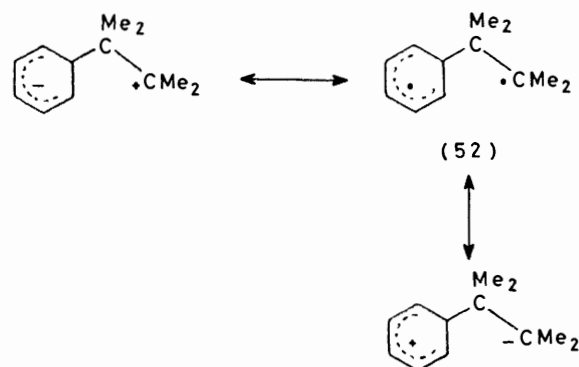
* The efficiency of *meta*-photocycloadditions of hydrocarbon ethylenes to anisole has been reported to be independent of solvent,³⁷ but the corresponding addition of ethyl vinyl ether to anisole is markedly enhanced by increase in solvent polarity.³⁸

addition was in general favoured when the reactants constituted a distinct donor-acceptor pair, otherwise *meta*-cycloaddition tended to predominate. This relationship is in general borne out by the results now described, but the additions of vinylene carbonate (I.P. 10.08 eV)⁴⁴ and ethylene and propylene (I.P. 10.5 and 9.73 eV, respectively)⁴⁵ have been reported to be anomalous. The reported preference of vinylene carbonate for *meta*-addition may be more apparent than real, for reasons which we have previously discussed,² and the preference of ethylene for *meta*-addition is in any case only slight, and possibly even non-existent to judge from the reported photolability of the *ortho*-adduct, and the absence of data for extrapolation to zero time.⁴⁵ Propylene appears to exhibit a greater propensity for *meta*-addition than does ethylene, in accordance with the dependence on ionisation potential which we have proposed, but since there were again no data for zero time, it is not possible to exclude the possible formation and subsequent photodissociation of a labile *ortho*-adduct in this system, as occurs with ethylene and benzene. The authors made the interesting suggestion that electron affinities may provide a better guide than ionisation potentials to the photochemical behaviour of alkenes in these systems,⁴⁵ but while this idea may have some merit, we note that the identical electron affinities of ethylene and propylene (E.A. - 1.8 eV) would not in themselves account for the differing behaviour which they report for these hydrocarbons. All this being said, the 8.65–9.6 eV range of ionisation potentials which we advanced as associated with a predominant tendency for *meta*- rather than *ortho*-cycloaddition was based on the results obtained with only seventeen ethylenic addends, and may well prove a little too restricted to cover all such addends. Nevertheless, the predictive value of the ionisation-potential relationship has been demonstrated in the further examples of vinyl acetate,⁴⁶ dihydropyran,⁴⁷ methyl acrylate and methyl methacrylate,⁴⁸ methyl crotonate,⁴⁹ and 1,1-dimethoxyethylene.⁴⁹ As yet we know of no exceptions to the general relationship whereby the tendency for an ethylenic compound to add *meta* rather than *ortho* to the benzene ring is associated with relatively small differences in ionisation potential between the addend and the aromatic compound.

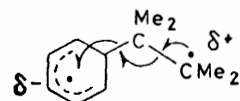
Further discussion of the ionisation potential relationship is provided later. Meanwhile, we draw attention to the following further features of the results listed in the Table. Among the cycloalkenes, cyclohexene is clearly anomalous in its reluctance to cycloadd to benzene and the marked tendency for dimerisation relative to the other addends. For the former we can advance no satisfactory explanation. The ionisation potential is closely similar to those of the alkenes which photoadd readily. Examination of models has revealed no unusual Baeyer or Pitzer strain in the adducts, and an n.m.r. spectroscopic investigation of ground-state complexation (see later) has indicated that cyclohexene behaves very similarly to *cis*-cyclo-octene in this respect.

As we have noted in the Results section, the cyclohexene dimers are exclusively of the cyclobutane type, and although there is evidence that they arise *via* triplet-benzene sensitisation, no evidence for the involvement of the highly strained *trans*-cyclohexene could be obtained: indeed the lack of stereospecificity argues against this intermediate.

The *para*-ene-addition has not been observed to occur with any of the cycloalkenes. Relative to *meta*-addition, it occurs with the methylethylenes in the increasing order $\text{Me}_2\text{C}=\text{CH}_2 < \text{Me}_2\text{C}=\text{CHMe} < \text{Me}_2\text{C}=\text{CMe}_2$, which is also the order of increasing donor character, and it does not apparently occur with either propylene⁴⁵ or the but-2-enes.⁵ The ene-addition is evidently favoured by increasing methylation of the ethylenic bond, and a CMe_2 group is present in each case where ene-addition has been found to occur. As noted in the Results section, the ene-addition of 2,3-dimethylbut-2-ene is non-stereospecific, and therefore evidently non-concerted. The promotion by proton donors and the incorporation of deuterium from MeOD in the 4-position are consistent with the formation of the intermediate (52)⁵⁰ or at least a corresponding polarised exciplex capable of acting as a proton acceptor. For a singlet species, as in the present case, little or no diradical character is likely (*cf.* benzyne), but a corresponding triplet species would be expected to exhibit reactivity more characteristic of a diradical.



Note that the above electron delocalisation involves an interaction between centres formally separated by an sp^3 hybridised carbon atom. The tendency for a hypothetical diradical form to polarise in a preferred sense can be represented as below.

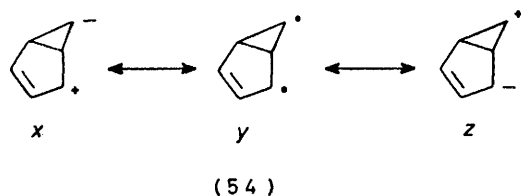
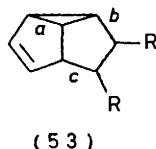


The stability of such a singlet intermediate species of the major left-hand canonical type (52), contrary to that of the lower form, would be favoured by dimethylation at the positive pole, and the apparent failure of propene and the but-2-enes to undergo ene-addition may in part be attributed to the absence of this structural feature.

The non-concerted character of photochemical *para*-ene-addition of alkenes to benzene is rather unexpected in view of the concerted nature normally attributed to conventional thermal ene-additions of alkenes,⁵¹ but the experimental evidence in the present cases appears unambiguous. The inapplicability of the Woodward–Hoffmann rules to photoprocesses involving benzene has previously been pointed out.¹⁰

Orbital Symmetry Aspects.—The results of an analysis of orbital symmetry relationships in photoadditions to the benzene ring have already been summarised,¹⁰ and the corresponding symmetry diagrams have been presented and discussed in refs. 2, 50, and 52. The conclusions most relevant to this work may be summarised as follows. (i) The *ss* and *sa* *ortho*-cycloadditions of the ethylenic bond to benzene are forbidden as concerted homopolar processes from S_1 benzene (${}^1B_{2u}$) plus S_0 ethylene, but allowed from S_0 benzene plus S_1 ethylene and from S_2 benzene (${}^1B_{1u}$) plus S_0 ethylene.

(ii) The corresponding *ss* *meta*-cycloadditions to give the adduct (53) are allowed from S_1 benzene plus S_0



ethylene regardless of whether a bond *a* between *meta*-carbon atoms in the ring develops prior to, synchronously with, or subsequent to formation of the bonds *b* and *c* to the ethylene. *meta*-Additions are stereospecific with respect to the ethylenic addend, so bonds *b* and *c* may be presumed to form synchronously, or nearly so. The case where bond *a* forms first involves formation of the prefulvene species (54): this is then captured by the alkene. Prefulvene may be formed in its singlet ground state adiabatically from S_1 benzene.⁴² It may be more realistic to depict prefulvene as a hybrid between dipolar canonical forms than as a diradical (54y) [*cf.* (52)]. Form (54x) seems likely to make a greater contribution to the hybrid than (54z); but triplet pre-fulvene would probably more have the character of (54y).

(iii) The photochemical *ss* *para*-cycloaddition of an ethylenic bond to benzene is subject to the same symmetry relationships as apply to the *ortho*-additions.

(iv) All the processes become allowed when they occur *via* charge-transfer.

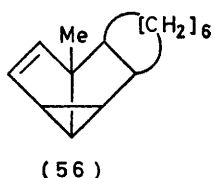
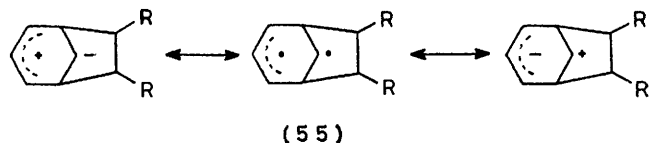
All the results obtained in this work accord remarkably well with the orbital-symmetry analysis. The experi-

mental conditions employed lead to excitation of the benzene rather than the alkene, so for reasons already given, the reactions can be considered to involve S_1 benzene plus S_0 alkene. In the cases where the difference in ionisation potential ($\Delta I.P.$) between the reactants is smallest, *i.e.* those where polar factors are least important, *meta*-cycloaddition tends to predominate: see Table. The insensitivity of *meta*-cycloaddition to solvent polarity is consistent with the essential homopolar nature of this process.* On the other hand, as $\Delta I.P.$ increases, *ortho*-cycloaddition tends to become more important relative to the *meta*-addition. It follows that *ortho*-cycloadditions would in general be expected to be favoured relative to the *meta*-processes by increased solvent polarity; and this effect has indeed been observed in several cases, most notably for the addition of 2,3-dimethylbut-2-ene to benzene (where $\Delta I.P.$ is greatest in the present series). Thus for the solvents cyclohexane and acetonitrile, the relative quantum yields *ortho/meta* were 1.0 and 1.75 ± 0.05 respectively in this system.

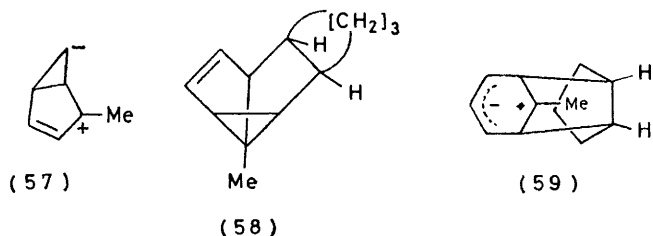
Thus in general, the *meta*-cycloadditions behave as homopolar processes whereas the *ortho*-reactions show distinct polar characteristics. The observed stereospecificity of *meta*-addition with respect to the alkene is readily explicable in terms of symmetry-allowed concerted processes, whereas the stereospecificity found in the formally non-concerted *ortho*-additions may reasonably be attributed to coulombic interactions between the reacting centres during the second stage of cycloaddition, whereby the configuration of the intermediate is effectively preserved. In fact, substantial stereoselectivity has previously been reported for photochemical cycloadditions between donor-acceptor pairs where concerted homopolar processes would be forbidden on orbital-symmetry grounds.⁵⁶ The *meta*-cycloadditions to benzene are decidedly remarkable, especially in view of the high quantum yields of some 0.3 found in certain systems (see Table). This facility may reflect the fact that *meta*-cycloaddition is the only concerted homopolar process which is available, and one moreover which is insensitive to the precise ordering of the bond-making steps. Thus vibrational excitation of S_1 benzene would give singlet prefulvene (54)^{42,55} in a symmetry-allowed process: this then either reacts with the alkene to give the *endo* and *exo-meta*-adducts or transforms into benzvalene and fulvene (these are not precursors of the *meta*-adducts^{56,57}). Alternatively, or concurrently, S_1 benzene may undergo direct *meta*-addition of an alkene (possibly *via* an exciplex, see below), giving an intermediate depicted as (55): *cf.* (52) and (54). This then undergoes intramolecular cyclisation to the *meta*-adduct(s).¹⁰ Although the

* Only one case has as yet been discovered where *meta*-cycloaddition exhibits sensitivity to solvent polarity, *i.e.* the 2,6-addition of ethyl vinyl ether to anisole.³⁸ The $\Delta I.P.$ is small (0.06 eV) so this predominant *meta*-addition accords with the above ionisation-potential relationship, but the solvent dependence is apparently anomalous, especially since the corresponding 2,6-photoaddition of 2,3-dimethylbut-2-ene to anisole shows no solvent dependence even though $\Delta I.P.$ is similar (0.2 eV).⁵³

results of the present work do not permit any clear distinction to be made between these mechanistic possibilities, it is unlikely that either in general occurs to the total exclusion of the other. Thus the pre-



fulvene mechanism would account nicely for the observation that the formation of fulvene from benzene in the liquid phase at 65 °C is strongly inhibited by the addition of even small proportions of *cis*-cyclo-octene,⁵⁸ yet is enhanced in alkane solvents.⁵⁹ It would also account for the preferred formation of isomer (56) in the photo-

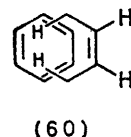


addition of *cis*-cyclo-octene to toluene, in that (57) would probably be the lowest-energy form of singlet methylpre-fulvene.¹¹ On the other hand, cyclopentene and toluene give (58) as the sole adduct detected,⁶⁰ a result difficult to reconcile with a prefulvene mechanism, but consistent with an alternative mechanism which involves the hypothetical intermediate (59) having a tertiary carbonium ion centre. It may well be that the mechanistic pathway followed in particular cases is critically determined by energetically minor steric factors which influence the orientation of complexation between the alkene and the aromatic ring. Such factors may also underlie the addition of cyclo-octene to give (56) as a 7 : 1 mixture of *endo* and *exo* isomers,¹¹ in contrast with the exclusively *endo* addition of cyclopentene to give (58).⁶⁰

para-Cycloaddition is evidently less common than the *ortho*-process (except with allenes⁶) even though it is subject to similar orbital-symmetry considerations. There is no apparent correlation with ionisation potential or ring size. Although *para*-addition might require greater distortion of the benzene ring from planarity in the transition state, this consideration does little or nothing to explain why cyclobutene has a proclivity for *para*-addition so markedly out of line with that of the other cycloalkenes. As with *meta*-addition, a solution to

this problem may well lie in factors which influence the stereochemistry of ground-state complexes or exciplexes between the reactants.

Complexation between Benzene and Alkenes.—Such complexation could in principle involve ground-state species and/or exciplexes. We have previously reported evidence from n.m.r. studies for the formation of *endo*-oriented ground-state complexes between benzene and various alkenes, *i.e.* *cis*- and *trans*-but-2-ene, *cis*-di-*t*-butylethylene, cyclopentene, cyclohexene, cycloheptene, *cis*- and *trans*-cyclo-octene, and norbornene: these systems exhibit no charge-transfer absorption.⁶¹ In each case, benzene induced small (*ca.* 5 Hz) downfield shifts of the vinyl protons and comparable upfield shifts of the allylic protons. *cis*-Di-*t*-butylethylene exhibited an 8 Hz downfield shift of the vinyl protons, but the resonance due to the eighteen methyl protons was largely unchanged (<1 Hz) possibly as a result of time-averaging.

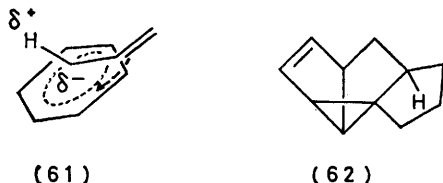


These results imply a preferred *endo* orientation between benzene and the alkenes, as depicted in (60). Other donor ethylenes such as vinyl ethers also appear to complex *endo* with benzene,⁶¹ although 2,2-dimethyl-1,3-dioxole is an exception,⁶² and the acceptor ethylenes so far examined complex in an *exo* orientation.⁶¹ We have previously drawn attention to the apparent similarity between the orientation in these 'dark' complexes and the stereochemistry of the corresponding *ortho*-additions: and it should be noted that *endo* rather than *exo meta*-adducts are also predominantly, or in some cases exclusively, formed between alkenes and benzene. It would appear that the stereochemistry of weak precursor 'dark' complexes between the reactants is an important factor in determining the stereochemistry of *ortho*- and *meta*-photoadducts. This cannot, however, be the only factor, for vinyl ethers such as ethyl vinyl ether, dihydrofuran, and 2,3-dihydro-1,4-dioxin form *endo* 'dark' complexes but give *exo ortho*-adducts^{47b} whereas methyl vinyl ketone, methyl acrylate, and methyl methacrylate yield mixtures of *exo* and *ortho*-cycloadducts.⁴⁸ The prior orientation of the reactants in 'dark' complexes may also be a factor in the apparently efficient trapping of prefulvene by some alkenes.

The reason for the preferred *endo* complexation between simple alkenes and benzene is far from clear, for this orientation would at first sight be expected to cause greater repulsive interactions than would be involved in *exo* complexation. For those alkenes having allylic hydrogen atoms, the donor character relative to benzene might give rise to weak π bonding between these δ^+ hydrogens and the benzene ring, as depicted in (61); but this could not account for the apparent *endo* orientation found for *cis*-di-*t*-butylethylene. It may be that the 'parallel' model (61) is not appropriate for this sterically

crowded alkene, and that the descreening of the vinyl protons results from a more orthogonal orientation which permits no significant overlap between the two π -electron systems. This might also explain why *cis*-di-*t*-butylethylene fails to photoadd to benzene.

We refer in conclusion to the possible involvement of exciplex intermediates in the photoadditions of alkenes to benzene. The involvement of exciplexes is of course well



established for many other photoaddition processes, so is a reasonable *a priori* postulate which has been discussed by several authors.^{5,60,63-65} Unfortunately, conclusive evidence on the matter is still lacking, largely because exciplex emission appears never to have been observed from benzene-alkene systems. Most of the discussion has tended to centre around Morrison's interesting proposal that a singlet intramolecular exciplex is formed on irradiation of 6-phenylhex-2-ene in solution as a precursor of the intramolecular *meta*-cycloadducts, *e.g.* (62).⁶³ Morrison's main grounds for proposing the involvement of an exciplex in this system were as follows: (a) the greatly reduced fluorescence intensity and singlet-state lifetime in comparison with those of 1-phenylhexane; (b) greater quenching of fluorescence than adduct formation by oxygen, piperylene, and acetone; (c) evidence that the adduct was derived from singlet rather than triplet precursors; and (d) analogy with $\text{Ar}[\text{CH}_2]_3\text{Ar}$ compounds which are known to exhibit excimer fluorescence.⁶⁶

Even if an exciplex is involved in the case of 6-phenylhex-2-ene (and this is still more a matter of probability than proof), it should be noted that the intermolecular additions exhibit certain features which differ from those of the intramolecular case. Firstly, intramolecular quenching of the aromatic fluorescence by the ethylenic moiety in 6-phenylhex-2-ene is quite strong (94% diminution in comparison with 1-phenylhexane), whereas the intermolecular quenching of benzene fluorescence by alkenes is feeble, and scarcely much greater than that by alkanes.⁴³ Such intermolecular quenching as does occur appears to increase with increasing methylation of the ethylenic bond, being greatest with 2,3-dimethylbut-2-ene in the series studied. This increase therefore more parallels the increase in donor character of the alkene than the quantum yield for *meta*-cycloaddition.

Secondly, despite the differences between intramolecular and intermolecular fluorescence quenching, and the formation of ground-state intermolecular complexes between alkenes and benzene, the corresponding quantum yields of adduct formation are closely similar in several cases (*ca.* 0.2–0.3).

Thirdly, the quantum yields of intramolecular adduct

formation increase with decreasing wavelength of irradiation within the $S_0 \rightarrow S_1$ band, whereas an opposite wavelength dependence has been reported for the gas-phase photoaddition of *cis*-but-2-ene to benzene.⁵⁷

These differences may be due in part to phase and concentration differences; but nevertheless they justify a certain prudent reserve against drawing close mechanistic analogies between the intra- and inter-molecular processes. However, since we have shown that weak intermolecular ground-state complexes are formed in solution, it would not be unreasonable to suppose that comparable exciplexes should be capable of existence. And insofar as intermolecular fluorescence quenching by the more donor alkenes such as 2,3-dimethylbut-2-ene could be expected to involve a degree of charge-transfer, some coulombic binding interaction within a transitory complex is to be expected. Although the significance, if any, of intermolecular exciplexes in the present systems, including those where $\Delta I.P.$ is small, remains an open question, a more interesting mechanistic point lies in the efficiency of alkene-benzene cycloaddition from S_1 benzene relative to the inefficiency of fluorescence quenching. More significantly, no consistent relationship is apparent between the donor character of the alkene and the efficiency of *meta*-cycloaddition (see Table). But as we have already pointed out, there is in general a greater relative tendency for *ene*- and *ortho*-addition with comparable alkenes of the greatest donor character, so as fluorescence quenching also appears related to the donor character, it may well be that the *ene*- and *ortho*-additions occur from the fluorescent state of S_1 benzene *via* an exciplex having dipolar character.

EXPERIMENTAL

All irradiations were performed in quartz tubes of varying capacity using light from Hanovia 15-W low-pressure mercury-arc lamps. Large-scale irradiations of the benzene-*cis*-cyclo-octene system were also carried out using a 400-ml capacity scraper cell and Hanovia 500-W medium-pressure arc lamps.^{15,*}

Quantum-yield measurements were all made on iso-octane solutions 1.1M in benzene and 3.5M in the ethylene under air at 20 °C, using radiation from a low-pressure lamp. Stirring or degassing the irradiated solutions caused negligible effects on the efficiency or linearity of adduct formation over a reasonable time period. The light intensity was measured by the method of Hatchard and Parker,⁶⁷ and checked repeatedly by a photocell. Product determination was by g.l.c.

Irradiation of Benzene and cis-Cyclo-octene.—The *cis*-cyclo-octene was freed from impurities absorbing at 254 nm by successive passage down silica (BDH silica 60—120 mesh, activated for 10 h at 120 °C) and alumina (Woelm Alumina Grade I) columns. A 3:1 v/v solution of the ethylene and benzene was irradiated for varying time periods according to the particular adduct mixture required (see text).

* *Note added in proof.* After this paper was submitted Scharf and his co-workers provided convincing evidence that the *meta*-addition of 2,2-dimethyl-1,3-dioxole to benzene proceeds *via* a fluorescent exciplex.⁷¹ In view of the fact that this fluorescence was only observed to occur in acetonitrile solution, the relevance of this work to the present systems remains to be clarified.

The *meta*-cycloadducts (3) and (4) were effectively removed from the 1:1 adduct mixture by shaking a light petroleum (b.p. 60–80 °C) solution containing *ca.* 1.0 g of the adducts (20 ml) with a saturated methanolic solution of mercuric acetate (50 ml) for 12 h. A further 50 ml of light petroleum was added to the mixture followed by 5 ml of distilled water. The above procedure was repeated twice on the resulting petrol layer and the final petroleum solution was found by g.l.c. (Carbowax 20M) to contain the *ortho*-cycloadduct (2) and longer retention-time products.

Preparation of Diels–Alder Adducts (5a–c).—The petroleum solution (concentrated to 5 ml) of the 1:1 adducts enriched in (2) as prepared above was treated with either *N*-phenylmaleimide (0.3 g) in diethyl ether (5 ml) or *p*-bromo-*N*-phenylmaleimide (0.4 g) in diethyl ether (10 ml). After standing the solutions for 24 h at 8 °C, the white crystals of the 1:1:1 adducts were filtered off. Recrystallisation was from acetone [Found for (5a): C, 79.4; H, 7.3; N, 3.8. $C_{24}H_{27}NO_2$ requires C, 79.9; H, 7.5; N, 3.9%. Found for (5b): C, 65.5; H, 5.9; N, 3.2. $C_{24}H_{26}BrNO_2$ requires C, 66.1; H, 6.1; N, 3.1%].

The maleimide adduct of (2) was prepared directly from the adduct mixture without enrichment. Thus 2 ml of the crude mixture was extracted with 75 ml of light petroleum. To the clear solution, maleimide (1 g) in diethyl ether (20 ml) was added and the mixture refluxed for 2 h, reduced in volume to 40 ml, and allowed to stand at 8 °C. After 72 h the white crystals were filtered off and recrystallised from acetone [Found for (5c): C, 76.0; H, 8.4; N, 4.9. $C_{18}H_{23}NO_2$ requires C, 75.7; H, 8.1; N, 4.9%].

Isolation of Adducts (3) and (4).—The major *meta*-cycloadduct (4) was obtained in >97% purity either by preparative g.l.c. (Carbowax 20M on Chromosorb) of the adduct mixture which had been heated under nitrogen at 200 °C for 1 h to convert (3) into (11), or by column chromatography of the irradiation product using petrol (b.p. 60–80 °C) as eluant and silica gel (Hopkins and Williams M.F.C.), which had been activated for 8 h at 100 °C, as the stationary phase. This latter procedure also gave a mixture of (3) and (4) which was 60% rich in the former, while the g.l.c. separation give a sample of (11) of 95% purity. The n.m.r. spectrum (100 MHz, CCl_4) of (4) had benzene-derived resonances at δ 5.60–5.32 (2 H, H-3 and H-4, $J_{3,4}$ 5.5, $J_{2,3}$ 2.3, $J_{4,5}$ 2.3, and $J_{2,4}$ *ca.* 1 Hz), 3.90–3.75 (1 H, H-5), 3.55–3.27 (1 H, H-1) 2.00–1.75 (1 H, H-8), and 1.60–1.50 (1 H, H-2): these assignments were confirmed from the n.m.r. spectrum of the corresponding adduct of C_6D_6 and *cis*-cyclo-octene. The *cis*-cyclo-octene derived resonances in (4) were at δ 2.55–2.27 (2 H, H-6 and H-7) and 2.0–1.0 (12 H, $[CH_2]_6$). A similar spectrum was obtained for the mixture containing 60% of (3).

Reaction of Adduct (4) with Phenyl Azide and Tetracyanoethylene.—Adduct (4) (0.1 g) and phenyl azide (0.2 g) were dissolved in benzene (2 ml) and refluxed for 45 min under nitrogen. The resulting light brown solution was reduced in bulk (*ca.* 1 ml) and light petroleum (b.p. 60–80 °C) was added to turbidity. Fine white needle-like crystals were produced on cooling at 80 °C for several days and were recrystallised from benzene–light petroleum and dried on a filter paper to give (6) (30 mg), m.p. 162–164 °C, melting accompanied by effervescence to give a yellow oil (Found: C, 78.30; H, 8.14; N, 13.65. $C_{20}H_{25}N_3$ requires C, 78.13; H, 8.20; N, 13.67%). The n.m.r. spectrum of (6) had no olefinic resonance but instead an AB quartet due to two protons (δ_A 4.4, δ_B 3.9, J_{AB} 8 Hz) was evident.

Adduct (4) (0.1 g) and tetracyanoethylene (0.1 g) were dissolved in benzene (5 ml) and refluxed for 3 h. The benzene was removed at water-pump pressure to give a black solid which was extracted several times with 5-ml portions of light petroleum (b.p. 100–120 °C). Needles of (8) were deposited when the petroleum solution was cooled in ice, and the product was filtered off, m.p. 213–214 °C (Found: C, 75.61; H, 6.52; N, 17.2. $C_{20}H_{20}N_4$ requires C, 75.95; H, 6.33; N, 17.72%). The n.m.r. spectrum again shows no olefinic protons.

Thermal Isomerisation of Adduct (3).—The conversion of (3) into (11) in the mixture of adducts could be achieved either as above at 200 °C or in the injection block of a g.l.c. machine at temperatures >250 °C. In either case, preparative g.l.c. yielded a sample of (11) of 95% purity. The n.m.r. spectrum of (11) (60 MHz, CCl_4) had resonances at δ 5.52 (2 H, sharp s with very weak outer lines), 5.27 (1 H, br s), 3.7–3.3 (1 H, vbr), 3.6–1.9 (4 H), and 8.5 (12 H, br s). Compound (11) obtained from C_6D_6 and *cis*-cyclo-octene, had no resonances below δ 3, thus establishing the origin of the olefinic and bisallylic protons. Significant absorptions in the i.r. spectrum (liquid smear) of (11) appeared at 1 610 and 1 640 (C=C stretching modes), 850 (out-of-plane C–H bending in a trisubstituted olefin), and 710 and 680 cm^{-1} (out-of-plane C–H bending of the cyclic disubstituted olefin). The compound in cyclohexane had no absorption maximum above 210 nm. Treatment of benzene solutions of (11) with common dienophiles did not reduce its concentration as estimated by g.l.c.

2:1 Benzene–cis-Cyclo-octene Adducts.—The fraction distilling at 140–145 °C and 0.5 mmHg, produced from prolonged irradiation of 1:3 v/v solutions of benzene and *cis*-cyclo-octene comprised essentially 2:1 adducts (Found: C, 90.20; H, 9.60. $C_{20}H_{26}$ requires C, 90.20; H, 9.80%). This was confirmed by high-resolution mass spectrometry. Noteworthy spectroscopic features of the mixture are presented in the text.

Photopolymerisation of Benzene.—Benzene (100 g) with either 0.35 mol % of cyclo-octene or 0.06 mol % of the (3) and (4) adduct mixture was irradiated with a 100-W medium-pressure mercury-arc lamp under N_2 for 100 h. The benzene was removed at water-pump pressure to leave *ca.* 1 g of a viscous oil. The oil was successively treated with 50-ml portions of hexane, acetone, benzene, and chloroform (fractions H, A, B, C respectively), and the solvents were removed at water-pump pressure. Fraction H was an oil, $M < 500$ (Mecholab Osmometer), A was a viscous gum, M *ca.* 750 (8 benzene units), and B and C were white solids, M *ca.* 1 500 (18 benzene units) and 2 000 (24 benzene units) respectively. Fraction C was insoluble in benzene and all darkened on heating above 200 °C.

Irradiation of Benzene and trans-Cyclo-octene.—A 10% v/v benzene and 30% v/v *trans*-cyclo-octene iso-octane solution (50 ml) was irradiated with two 15-W low-pressure mercury lamps until the *ortho*-photocycloadduct (15) had reached its stationary concentration as judged by g.l.c. (Carbowax 20M). The starting materials were removed at water-pump pressure at <60 °C to yield a golden oil (*ca.* 1 ml). The combined products of three such irradiations were extracted with light petroleum (b.p. 60–80 °C) (30 ml) and the polymer filtered off. To the filtrate, which contained approximately equal quantities of (15), (17), and (18) (g.l.c.), *p*-bromo-*N*-phenylmaleimide (0.3 g) in benzene–diethyl ether (1:1) (10 ml) was added. The solution was shaken for 5 min and the mixture left to stand for 24 h at 8 °C. The

crystals of (16) (m.p. 273—274 °C) were recrystallised from acetone and had $M^+ = 440$ with major fragmentations at m/e 330, 252, and 198 (Found: C, 66.0; H, 5.95; N, 3.15. $C_{24}H_{26}BrNO_2$ requires C, 65.5; H, 5.9; N, 3.2%); δ (100 MHz, $CDCl_3$) 7.51 (2 H, d, J 10 Hz, *m*-H), 7.05 (2 H, d, J 10 Hz, *o*-H), 6.3—6.4 (2 H, dd, J 10 and 2 Hz, olefinic), 3.27 (2 H, br s, allylic H), 3.83 (2 H, s), 2.7—2.1 (2 H, m), and 2.0—0.5 (14 H, m).

Prolonged irradiation of the benzene-*trans*-cyclo-octene system gave essentially a two-component mixture of 1 : 1 adducts. The distilled mixture (80—85 °C at 0.1 mmHg) had i.r. and n.m.r. spectra virtually identical with those of the *meta*-cycloadducts found from the *cis*-olefin, and the pyrolysis product (19) had similar spectra to those of (11).

Irradiation of Benzene and Cyclopentene, Cycloheptene and cis-Cyclononene.—Preparative-scale irradiations of the above systems were performed using 2 : 1 v/v olefin-benzene solutions. The starting materials were removed at water-pump pressure and the resulting yellow oil was distilled at 0.1 mmHg. The major component(s) had spectroscopic properties very similar to those of (4) from benzene and *cis*-cyclo-octene described above. The amounts of the minor reaction components precluded their isolation, but some evidence concerning their structures was obtained by mass spectrometry, their thermal labilities, and their reactivities with dienophiles.

Irradiation of Benzene and Cyclohexene.—A solution of benzene (6 ml) and cyclohexene (54 ml) was irradiated in a quartz tube with low-pressure lamps for 16 h. The golden yellow solution yielded an oil (*ca.* 0.8 ml), b.p. 75—87 °C at 0.2 mmHg, after removal of the solvents. By mass-spectrometry-g.l.c. the mixture was deduced to comprise *ca.* 30% olefin dimers and 70% benzene-cyclohexene adducts. Irradiation of benzene (180 ml) and cyclohexene (20 ml) for 24 h yielded a golden oil (*ca.* 4 ml), b.p. 73—77 °C at 0.2 mmHg, which contained essentially only the three olefin dimers. The ratios of dimeric products are given in the main text. Formation of the cyclohexene dimers (24), (25), and (26) was carried out as outlined in ref. 26. Irradiation of benzene and cyclohexene in a methylcyclohexene-isopropanol glass at -70 °C was carried out in a Beckmann R11C Variable Temperature I.R. Unit fitted with CsBr windows and using a medium-pressure mercury arc.

Irradiation of Benzene and Cyclohexene in the Presence of Furan.—A mixture of benzene (45 ml), cyclohexene (5 ml), and furan (5 ml) was irradiated with two low-pressure Hg lamps for 16 h. The starting materials were removed from the golden yellow solution at water pump pressure to give *ca.* 1 ml of an oil, which distilled at 68—83 °C and 0.2 mmHg. The major cyclohexene-furan adduct was isolated by preparative g.c. (Carbowax 20M) of the mixture from several irradiations, and this was subsequently further purified from a minor contaminant (not detected by g.l.c.) by preparative t.l.c. using $AgNO_3$ -impregnated (1 g) silica (Hopkins & Wilkins SG40) (7 g) plates (7.5 × 2.5 cm) with benzene-diethyl ether (3 : 1) as eluant (major component $R_F = 0.13$; contaminant, R_F 0.45). N.m.r. spectrum of the purified oil (60 MHz CCl_4); δ 6.55 (1 H, dd, J 2 and 6 Hz), 6.18 (1 H, t, J 0.5 Hz), 5.90 (1 H, dd, J 2 and 6 Hz), 4.65 (1 H, br s), 4.40 (2 H, s), and 2.0—1.0 (8 H, br); ν_{max} . (liquid film) 2 930s, 1 720m, 1 600m, 1 460, 1 450m, 1 055m, 905s, and 690m cm^{-1} .

Irradiation of Benzene and Cyclobutene.—A solution (100 ml) of cyclobutene in benzene (10% v/v) was sealed in a

quartz tube and irradiated with two low-pressure mercury arcs as above at room temperature for 24 h. Removal of the starting materials at water-pump pressure at 40 °C gave *ca.* 2 ml of the *meta*- and *para*-cycloadducts (b.p. 46—48 °C at 2.0 mmHg) of cyclobutene with benzene, ratio *ca.* 9 : 1 respectively. The adducts were separated by preparative g.c., and their properties were in agreement with those reported by Srinivasan.²⁹

Oxidation of the para-Cycloadduct of Benzene and Cyclobutene.—The adduct (0.056 g) was heated on a steam-bath for 3.5 h with concentrated nitric acid (1.0 ml). Water (2.0 ml) was added to the brown solution and after heating for a further 2 h the solution was subjected to continuous ether extraction for 16 h. The ethereal solution was dried with anhydrous magnesium sulphate, and an ethereal solution of diazomethane was added until a permanent bright yellow colour was obtained. The solution was concentrated and g.c. and combined mass-spectrometry-g.c. showed that only the *cis*-isomer of the dimethyl ester of cyclobutane 1,2-dicarboxylic acid was present. Reference samples of the *cis*- and *trans*-isomers of the diester were synthesised by the method of Fonken and Shienthong.³⁰

Irradiation of Cyclopropene and Benzene.—The cyclopropene was synthesised by the method of Closs and Krante,⁶⁸ and was identified as its adduct with cyclopentadiene.⁶⁹ Cyclopropene (2.5 ml) was distilled into benzene (40 ml) which had been previously purged with nitrogen for 30 min. The solution was irradiated in a quartz tube with low-pressure lamps for 24 h, after which the reactants were removed at water-pump pressure to give *ca.* 0.5 ml of a yellow oil, which was analysed by g.l.c. and mass-spectrometry-g.l.c.

Synthesis of (32).—Maleic anhydride (11.1 g) and cycloheptatriene (10.0 g) were heated in refluxing xylene (40 ml) for 5 h. The solvent was removed (100 °C, 15 mmHg) and the yellow solid digested with diethyl ether (20 ml) and recrystallised from hexane (m.p. 99 °C). The procedure for decarboxylation of (32) was essentially that described by Westberg and Dauben⁷⁰ and the product was purified by preparative g.l.c. The irradiation of (32) (20 mg) was performed in benzene solution (1 ml) in a quartz tube using low-pressure Hg lamps, and was monitored by g.l.c.

Irradiation of 2,3-Dimethylbut-2-ene and Benzene.—As outlined in the text the ratios of the 1 : 1 adducts in this system varied with reactant concentration and irradiation time. From irradiation of 2,3-dimethylbut-2-ene (12 ml) in benzene (105 ml), *ca.* 1.5 ml of the adduct mixture (b.p. 50—55 °C at 2.5 mmHg) was obtained. Treatment of the adduct mixture (0.5 g), which contained *ca.* 12% of (38), in benzene (2.0 ml) with maleic anhydride (0.036 g) for 24 h yielded, after evaporation of the benzene and addition of light petroleum (b.p. 60—80 °C) (2.0 ml), an off-white solid which was sublimed at 120 °C and 0.1 mmHg to give a white solid (0.026 g), m.p. 192—193 °C (Found: C, 73.81; H, 7.86. $C_{16}H_{20}O_3$ requires C, 73.85; H, 7.69%); M^+ 260; δ (60 MHz, $CDCl_3$) 6.6—6.4 (2 H, vinylic t, J 3.5 Hz), 3.5—3.1 (2 H, allylic, m), 3.1—2.95 (2 H, protons on anhydride bridge, four couplings all 1.7 Hz), 2.25—2.15 (2 H, cyclobutene protons, four couplings all 1.7 Hz), 1.05 (6 H, s, *exo*-Me), and 0.82 (6 H, s, *endo*-Me).

The other two 1 : 1 adducts were isolated by preparative g.l.c.; the spectroscopic properties of the *meta*-cycloadduct were identical with those reported earlier. The third adduct was always somewhat contaminated by an aromatic impurity to which it could be thermally converted, and the

structures of (37) and (41), respectively, for these compounds were deduced principally from n.m.r. spectroscopic data (100 MHz, CDCl_3); (37) δ 5.82—5.40 (4 H, vinylic, J_{vic} 11 Hz), 4.76—4.64 (2 H, terminal vinylic, J_{allylic} 1.5 and 0.8, J_{gem} 0.8 Hz), 2.92—2.68 (1 H, bis-allylic methine, m), 2.76—2.46 (2 H, bis-allylic methylene, m), 1.76—1.72 (3 H, br s, allylic Me), and 0.98 (6 H, Me); (41) δ 7.28—7.10 (5 H, aromatic), 4.94—4.9 (1 H, terminal vinylic, J_{gem} 1.5, J_{allylic} 0.8 Hz), 4.84—4.78 (1 H, terminal vinylic, J_{allylic} 1.5 Hz), 1.48 (3 H, allylic Me), and 1.38 (6 H, Me).

The study of solvent effects on this system was performed on samples (0.5 ml) of a 10% v/v solution of 2,3-dimethylbut-2-ene in benzene in cyclohexane, diethyl ether, methanol, or acetonitrile (0.5 ml).

Irradiation of 2,3-Dimethylbut-2-ene and Toluene.—A 10% v/v solution (200 ml) of 2,3-dimethylbut-2-ene in toluene was irradiated for 48 h to give after work-up a yellow oil (ca. 2.0 ml). Preparative g.l.c. (Carbowax 20M) of the oil gave the 'ene'-product (45), purity >90%; δ (60 MHz, CDCl_3) 5.8—5.6 (2 H, m, vinylic), 5.4—5.2 (1 H, m, vinylic), 4.85—4.7 (2 H, m, terminal ethylene), 2.9—2.3 (3 H, m, bis-allylic protons), 1.8—1.75 (3 H, br s, vinylic Me), 1.75—1.6 (3 H, m, vinylic Me), and 0.95 (3 H, s, Me).

Irradiation of 2-Methylbut-2-ene and Benzene.—A solution of the ethylene (6 ml) and benzene (54 ml) was nitrogen-purged and irradiated in a quartz tube with a low-pressure lamp for 24 h, and product formation was monitored by g.l.c. (Carbowax 20M) (see text). The oil produced on removal of the starting materials at water-pump pressure was subjected to preparative g.l.c. and the major two components collected in >94% purity. The more abundant component eluted [benzene-diethyl ether (9:1)] on silver nitrate-impregnated ($12\frac{1}{2}\%$ t.l.c. silica gel (Whatman SG41) plates, followed by charring, showed four spots (R_F 0.24—0.27) of ca. equal intensity. The mixture was considered to comprise the four *meta*-cycloadducts on the basis of its spectroscopic and t.l.c. properties; λ_{max} (cyclohexane) 223 nm; δ 5.7—5.3 (2 H, m, vinylic), 2.8—2.5 (2 H, m), 2.0—1.4 (3 H, m), and 1.1—0.6 (9 H, m, Me).

Pyrolysis of this adduct mixture at 250—300 °C in the injection block of the g.l.c. resulted in the formation of a new low-retention-time 1:1 adduct ($M^+ = 148$) at the expense of ca. 25% of the *meta*-cycloadducts. The new product was collected in 95% purity; δ (60 MHz, CDCl_3) 5.55 (2 H, br s, vinylic), 5.1 (1 H, br s, vinylic), 3.8—3.4 (1 H, m, bis-allylic), 2.8—2.1 (3 H, m, allylic CH_2 and H β to vinyl), 1.6 (3 H, t, vinylic Me), 1.05 (3 H, s, Me), and 0.95 (3 H, s, Me). The remainder (75%) of the mixture was recovered unchanged as judged by t.l.c. and n.m.r. spectroscopy.

N.m.r. spectrum (60 MHz, CDCl_3) of the 'ene'-product (47); δ 5.6 (4 H, br s, vinylic), 4.9—4.6 (2 H, m, terminal vinylic), 3.0—2.4 (3 H, m, bis-allylic H), 2.4—1.9 (1 H, m, allylic methine), 1.8 (3 H, t, vinylic Me), and 1.05—0.95 (3 H, d, allylic Me).

Irradiation of 2-Methylpropene and Benzene.—2-Methylpropene was bubbled through benzene (50 ml) which had been previously purged with nitrogen, until there was a 5% increase in volume. The solution was then irradiated in a quartz tube for 24 h. The two *meta*-cycloadducts (49) and (50) and the 'ene'-product (51) were isolated by preparative g.l.c. in ca. 95% purity from the combined products of several irradiations. For both (49) and (50); λ_{max} (cyclohexane) 220 nm; and ν_{max} (liquid film) 3 040, 1 600, and 720 (vinylic) cm^{-1} . N.m.r. spectrum (60 MHz, CDCl_3) of (49), δ 5.7—5.2 (2 H, m, vinylic) 3.2—2.9 (1 H, m, allylic),

2.8—2.3 (1 H, m), 2.2—1.7 (1 H, m), 1.8—1.5 (1 H, m, cyclopropyl allylic), 1.5—1.2 (2 H m methylene), 1.15 (3 H, s, Me), and 1.1 (3 H, s, Me). N.m.r. spectrum (60 MHz, CDCl_3) of (50) was not so well resolved as that of (49); δ 5.7—5.3 (2 H, m, vinylic), 2.7—2.3 (2 H, m), 2.0—1.3 (4 H, m), 1.10 (3 H, s, Me), and 0.85 (3 H, s, Me).

Heating (50) at 250—300 °C converted this adduct into an isomer ($M^+ = 134$), δ (60 MHz, CDCl_3) 5.7—5.2 (4 H, m, vinylic), 3.9—3.5 (1 H, m, bis-allylic), 2.7—2.1 (3 H, m, allylic CH_2 and β -methine), 1.07 (3 H, s, Me), and 1.00 (3 H, s, Me).

The minor product from irradiation of this system was identified as the 'ene'-product (51) from its spectral properties and comparison with those of similar structure [e.g. (37) and (47)]; (51), δ (60 MHz, CDCl_3) 5.6 (4 H, br s, vinylic), 4.9—4.5 (2 H, m, terminal vinylic), 3.0—2.4 (3 H, m, bis-allylic methylene and methine), 2.2—1.9 (2 H, m, allylic methylene), and 1.7 (3 H, m, vinylic Me).

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