

## Intramolecular Photocycloaddition Reactions of Phenyl-Vinyl Bichromophoric Systems

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The intramolecular photocycloaddition reactions of several phenyl-vinyl bichromophoric systems are reported. 5-Phenylpent-1-ene and allyl benzyl ether both yielded *meta*-cycloadducts derived from 1,3- and 2,6-attack of the vinyl group on to the phenyl moiety, whereas 3-phenylpropyl vinyl ether and 2-phenoxybut-1-ene gave products which reflected 1,3- and 2,4-, and 2,4-attack, respectively. In contrast, the major mode of reaction from phenethyl vinyl ether involved 2,5-cycloaddition and the 1,4-intramolecular cycloadduct structure was assigned to the sole photoisomer of 2-phenoxyethyl vinyl ether. Quantum efficiencies were very variable ranging from 0.005 to 0.11; polymeric materials were formed in all cases and were the major products from the two phenoxy-compounds. The reactions are discussed in terms of previous mechanistic proposals for benzene-ethylene photocycloaddition processes and conformation of the excited-state molecules.

In recent years there has been considerable interest in the intramolecular excited-state interactions and reactions of non-conjugated bichromophoric molecules.<sup>1</sup> Yet despite an extensive literature concerning photocycloaddition reactions of benzene-ethylene systems,<sup>2,3</sup> prior to the present studies,<sup>4</sup> the corresponding intramolecular addition process was restricted to two reported examples involving *cis*- and *trans*-6-phenylhex-2-enes<sup>5</sup> and the Diels-Alder adduct of 1,4-naphthoquinone and cyclopentadiene.<sup>6</sup> The type of photoadduct formed from these systems was that expected from a consideration of intermolecular analogues in the former case<sup>2,7</sup> and that dictated by molecular geometry of the starting material in the latter example. From photophysical studies of the 6-phenylhex-2-enes, it was proposed that the observed *meta*-intramolecular cycloaddition originated from a phenyl-ethenyl exciplex<sup>5</sup> and this postulate has been extended to include the intermolecular cycloadditions of benzene and its derivatives with ethylenes,<sup>8,9</sup> but in such systems, it is only with 1,2-dialkoxyethylenes and benzene in acetonitrile solution that emission from an excited-state complex has been observed.<sup>10,11</sup>

In the present paper we describe the photochemical reactions of bichromophoric ethers of type (1) and compare these with those of 5-phenylpent-1-ene.<sup>4</sup> The findings are discussed in relation to the number and types of intervening groups between the chromophores, conformations of excited state intermediates, and the previous mechanistic proposals for intermolecular benzene-ethylene photocycloaddition reactions.

### RESULTS

Vinyl compounds in general undergo photoaddition to benzene less readily than 1,2-disubstituted ethylenes but were chosen for the present study as they avoid problems arising from ethylene *cis-trans*-isomerisation and possible differing photoreactivities of the geometrical isomers. Some fluorescence data for 5-phenylpent-1-ene, the hydrocarbon 'standard' for the present study, have been described<sup>5</sup> but its photochemistry has not been reported. Details of irradiation conditions are given in the Experimental section but degassing of solutions had little effect on yields or product ratios and preparative experiments were

generally performed under air. Spectroscopic and chemical features of the products of benzene-ethylene irradiations which allow conclusive structural assignments and a distinction to be made between *ortho*-, *meta*-, and *para*-cycloadduct structures are well documented<sup>8,9,12,13</sup> and hence such aspects of the present systems are not described in detail here. Considerations of molecular models of adduct structures which may arise from the present intramolecular cycloadditions allowed some structures to be discounted because of their highly strained or impossible geometries caused by the unit originally joining the chromophores. Numbering of the *meta*-cycloadducts is that given in (2) and it will be noted that the unit originally joining the chromophores must now be between the 6- or 7-positions and the 1-, 2-, 3-, 4-, 5-, or 8-positions.

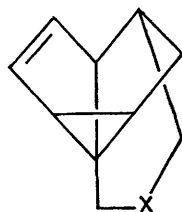
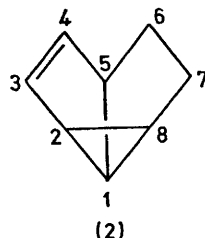
**5-Phenylpent-1-ene.**—Irradiation of a 1% solution of 5-phenylpent-1-ene in cyclohexane solution gave three photoisomers ( $M^+$  146 m.u.; m.s.-g.l.c.) in a time-independent ratio of ca. 1 : 1 : 5 (g.l.c. elution sequence, Carbowax 20M). The proportion of the major isomer was very dependent upon the temperature of the g.l.c. analysis and at injection-port temperatures of 300 °C was quantitatively converted into an isomer of much shorter retention time than the photoisomers. The major photoisomer was separated from the reaction mixture by preparative g.l.c. with >95% purity (g.l.c.). From a comparison of the <sup>1</sup>H n.m.r. spectrum of this photoisomer with those of *meta*-cycloadducts and in particular those reported from 6-phenylhex-2-enes,<sup>5</sup> it was deduced that the vinyl group had undergone 2,6-intramolecular photocycloaddition to the phenyl group to give (3). Significant in the spectral interpretation was the presence of the typical AB quartet for the ethenyl protons of *meta*-cycloadducts with both sets of allylic couplings and the absence of the H-1 triplet ( $J_{1,2} = J_{1,5} = J_1 = 7$  Hz<sup>9</sup>) at  $\delta$  ca. 2.2. Because of geometrical constraints, the trimethylene bridge must be to the 6-*exo*-position of (3).† Use of high injection-port temperatures on preparative g.l.c. caused the conversion of (3) into its thermal isomer which was then separated with >99% purity (g.l.c.). The <sup>1</sup>H n.m.r. spectrum showed the presence of four ethenyl protons and ten protons on saturated carbon atoms and from further analysis, structure (5) was assigned to this thermal isomer. *meta*-Cycloadducts

† Throughout this paper, *exo* and *endo* refer to the orientation of the substituent with respect to the 3,4-double bond in these structures.

with an *endo*-hydrogen at the 7-position are well known to yield bicyclo[3.3.0]octa-2,7-diene derivatives by a 1,5-sigmatropic shift<sup>14</sup> and hence the assignment of (5) to the thermal isomer confirms the 6-*exo*-structure (3) for its precursor. The rearrangement in the present case took place

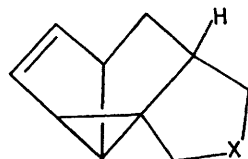


- (1)  $a; x = 2, y = 0$   
 b;  $x = 3, y = 0$   
 c;  $x = 0, y = 2$   
 d;  $x = y = 1$



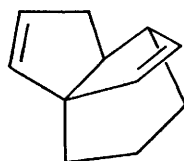
(3)  $X = \text{CH}_2$

(4)  $X = \text{O}$

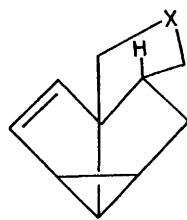


(6)  $X = \text{CH}_2$

(7)  $X = \text{O}$



(5)



(8)  $X = \text{CH}_2$

(9)  $X = \text{O}$

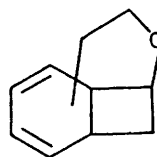
readily and at 150 °C after 1 h (3) was 50% converted into (5). Structure (3) for the major photoisomer of 5-phenylpent-1-ene is analogous to that assigned to the sole intramolecular adduct from *trans*-6-phenylhex-2-ene.<sup>5</sup>

Separation of the minor photoisomers from the present system was achieved by preparative g.l.c. with only 60% purity (g.l.c.), the impurity being (5), but analysis of the <sup>1</sup>H n.m.r. spectra and in particular the ethenyl proton resonances did allow structural assignments to be made. Both photoisomers had resonances characteristic of *meta*-cycloadducts. The shorter retention time product had no substitution on the ethenyl grouping (*i.e.* H-3 and H-4 present) and these proton resonances showed both allylic couplings; hence the alkyl chain was not on the 2- or 5-positions. The isomer substituted at the 1-position was assigned to the major photoproduct; hence this minor product must be substituted at the 8-position of (2) and molecular models showed that the 7-*exo*-isomer (6) was that most favoured. The <sup>1</sup>H n.m.r. spectrum of the second minor isomer again showed the presence of two ethenyl protons but the 2-Hz coupling of the higher-field doublet of the AB quartet was absent, thus showing that the 5-position in (2) was substituted and hence the trimethylene chain was from C-5 to C-6; again models suggested *exo*-stereochemistry at C-6 and thus (8) is assigned to this photoisomer. The assignments of (6) and (8) were supported by the close

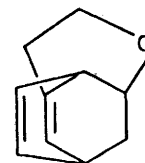
similarity of their spectra with those of the 6-*exo*-methyl isomer of (6) and the 7-*exo*-methyl isomer of (8), respectively, which were the two photoisomers formed with equal efficiency from *cis*-6-phenylhex-2-ene.<sup>5</sup> Irradiation of solutions of 5-phenylpent-1-ene always produced amounts of polymeric materials which were reflected by quantum-yield data; thus, whereas that of the disappearance of starting material was 0.42, those of the formation of (6), (8), and (3) were 0.02, 0.023, and 0.11 respectively.

**Phenylalkyl Vinyl Ethers.**—Irradiation of phenyl vinyl ether in either polar or non-polar solvents or in the vapour phase produced polymeric materials and only traces (<1%) of volatile products which were not further examined but did not contain styrene oxide or 2,3-dihydrobenzofuran. Benzyl vinyl ether as a 1% solution in cyclohexane gave on irradiation an almost quantitative yield of β-phenylpropionaldehyde as earlier reported by Pinhey and Schaffner<sup>15</sup> but phenethyl vinyl ether (1a) and 3-phenylpropyl vinyl ether (1b) gave photoisomers.

Irradiation of (1a) as a 1, 5, or 10% solution in cyclohexane yielded two photoisomers ( $M^+$  148 m.u.; m.s.-g.l.c.) but one of these was labile under the conditions of its formation. At conversions of (1a) of <0.1% the ratio of photoisomers was *ca.* 1 : 40 (g.l.c. elution sequence on 9% Apiezon L/2% KOH columns) whereas at 10% conversion the ratio was 1 : 5. Neither the yield nor the ratio of the photoisomers was significantly affected by change of reaction solvent to ethyl acetate, acetonitrile, or methanol although, as expected, variable amounts of 2-phenylethanol and 1-methoxy-1-(2-phenethoxy)ethane were produced from (1a) in methanol. The two photoisomers had similar mass spectra although ions of 117 (loss of OCH<sub>3</sub>) and 133 m.u. (loss of CH<sub>3</sub>) were four times as abundant in the major than the minor product. Both isomers were unaffected by *N*-phenylmaleimide under conditions which yield Diels-Alder adducts from the *ortho*-cycloadducts of ethyl vinyl ether with benzene or toluene<sup>13</sup> thus demonstrating the absence of a *cis*-1,3-diene unit as in (10), a product which may have been expected by analogy with



(10)

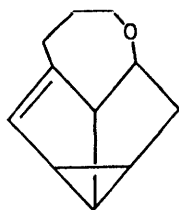


(11)

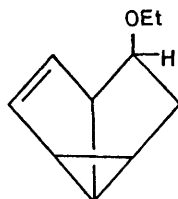
the above intermolecular reactions. The major photoisomer was converted back into (1a) both photochemically and thermally, and this latter lability prevented its isolation by preparative g.l.c. in >85% purity. Such retroadditions<sup>8</sup> are, however, wholly consistent with structure (11) for this isomer which was assigned essentially by analysis of its <sup>1</sup>H n.m.r. spectrum and this was greatly aided by the addition of Eu(fod)<sub>3</sub> and subsequent spin-decoupling experiments. The minor photoisomer of (1a) was separated with only 50% purity (g.l.c.) but since the other 50% was phenethyl vinyl ether, a subtracted <sup>1</sup>H n.m.r. spectrum was easily obtained. The spectrum was consistent with that of *meta*-cycloadducts and had a ratio of ethenyl protons to protons on saturated carbons of 1 : 5. The multiplicity of the former resonance was the characteristic AB quartet but the H<sup>4</sup>-H<sup>5</sup> coupling of the higher-field half of the resonance was absent again showing substitution at the 5-

position and *exo*-stereochemistry was deduced at C-6 because of the considerable strain in the tetrahydrofuran unit which an *endo*-orientation would involve. Hence this product was analogous to (8) from 5-phenylpent-1-ene and one of the photoisomers of *cis*-6-phenylhex-2-ene, but unlike the hydrocarbons no 7,8-substituted product of (2) was observed from (1a). The quantum yields for formation of the major and minor photoisomers of (1a) were determined as 0.23 and 0.006, respectively.

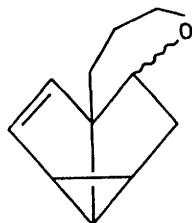
Irradiation of 1% solutions of 3-phenylpropyl vinyl ether (1b) in cyclohexane gave low yields of three photoisomers ( $M^+$  162 m.u.; m.s.-g.l.c.) in an essentially time-independent ratio of ca. 1:1:15 (g.l.c. elution sequence, Apiezon L/KOH columns). Prolonged irradiation of the system gave minor amounts of a compound of molecular weight 182, which, following isolation and spectral analysis, was deduced to be dicyclohexyl ether; in the present study, only with (1b) and 2-phenoxyethyl vinyl ether was this reaction product observed and its genesis was not investigated. The major photoisomer from (1b) was isolated with 99% purity (g.l.c.) by preparative g.l.c. and from its  $^1\text{H}$  n.m.r. spectral data was assigned structure (12) which reflects 2,4-intramolecular ethylene attack on the phenyl ring. This orientation of attack is uncommon in *meta*-cycloadditions but the structure was deduced in the present case essentially from the presence of only one ethenyl proton which was coupled to H-2, the simplicity of the H-5 resonance (6 Hz triplet at  $\delta$  2.85), and the very close similarity between the double doublet centred at  $\delta$  4.45 in this spectrum and the resonance of H-6 in the 6-*endo*-ethoxy *meta*-cycloadduct (13) from benzene and ethyl vinyl ether. The effect of  $\text{Eu}(\text{fod})_3$  on the spectrum, interpreted by through-bond and across-space effects of the europium atom, was wholly consistent with this assignment; molecular models also indicated that *exo*-stereochemistry at C-6 was highly unfavoured. The minor photoisomers of



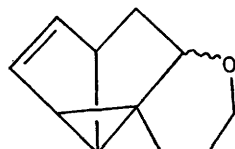
(12)



(13)



(14)

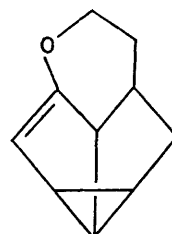


(15)

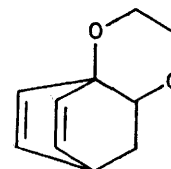
(1b) formed in a 1:1 ratio were isolated in 75 and 65% purities (g.l.c.) with the 'impurities' being the starting material; both were deduced to be *meta*-cycloadducts. From analysis of the  $^1\text{H}$  n.m.r. spectrum of the shortest retention time isomer it appeared that minor amounts of a second intramolecular *meta*-cycloadduct were present, but

from the simplicity of the higher-field half of the ethenyl proton resonance in the major product, the C-5 position was deduced to be substituted and hence the unit originally joining the chromophores was now between the 5- and 6-positions of (2) as in structure (14). The stereochemistry about C-6 could not be unambiguously assigned by further spectral analysis and molecular models indicated that the tetrahydropyran ring for either *exo*- or *endo*-stereochemistry at C-6 may exist in a chair conformation and it may well be that both stereoisomers of (14) were formed. Similarly, although it was deduced from the  $^1\text{H}$  n.m.r. spectrum of the other minor photoisomer of (1b) and its comparison with the spectrum of the 7-ethoxy-isomers of (2) from benzene and ethyl vinyl ether that this product had structure (15) with the trimethyleneoxy-chain between the 7- and 8-positions, no decision concerning the stereochemistry about C-7 could be made and again in both stereoisomers it appeared from molecular models that the tetrahydropyran ring could adopt a chair conformation. The quantum yield for disappearance of (1b) was 0.1 and those for formation of (14), (15), and (2) were 0.005, 0.007, and 0.05 respectively.

**4-Phenoxybut-1-ene (1c).**—Irradiation of this ether as a 1% solution in cyclohexane produced large amounts of polymeric material, which was periodically removed by filtration, and a slow conversion into one photoisomer ( $M^+$  148 m.u.) which, unlike (1c), had a very prominent parent ion (ca. 80% of base ion at 94 m.u.). In view of the small amounts of product and separation difficulties, it proved practicable to obtain the isomer only as a 3:2 mixture with (1c). Nevertheless by a subtractive procedure with the  $^1\text{H}$  n.m.r. spectrum, some structural assignment was made.



(16)



(17)

Thus only one ethenyl proton resonance (triplet) was evident, centred at  $\delta$  5.5, and the appearance of this was essentially identical with that of the H-3 proton resonance of (12); the move to lower field of this resonance in the present case was attributed to the proximity of the ethereal oxygen. The presence of an enol ether grouping was confirmed by the  $1680\text{ cm}^{-1}$  absorption in the i.r. spectrum. Thus substitution at the 4-position of (2) was deduced. Molecular models indicated that an ethoxy-bridge can only span from the 4-position of (2) to the *endo* 6- or 7-positions and that the latter produces a highly strained system. Thus we tentatively assigned structure (16) to the photoisomer of (1c). The very low yields of (16) and the rapidly formed heavy polymeric deposits made meaningful quantum-yield determinations impracticable in the present case.

**2-Phenoxyethyl Vinyl Ether.**—As with the foregoing phenoxy-compound, irradiation of 2-phenoxyethyl vinyl ether produced much polymer and it was estimated by g.l.c. that following 14 days reaction <5% of the starting material was converted into volatile products; the remain-

ing 95% had polymerised. Analysis of the volatile fraction revealed the presence of three products, one of which was dicyclohexyl ether (m.s. and g.l.c.), another which had no clear parent ion but which from the fragmentation pattern in the mass spectrometer was deduced to have a cyclohexyl group and hence was solvent derived, and the third was a photoisomer ( $M^+$  164 m.u.) of 2-phenoxyethyl vinyl ether. The photoisomer was photochemically and thermally labile and was isolated as a 2:3 mixture (g.l.c.) with the starting material. The  $^1\text{H}$  n.m.r. spectrum of this mixture revealed that the photoisomer had four ethenyl protons in the  $\delta$  5.7–6.5 region. From this datum, the lability of the product,<sup>8</sup> and its lack of reaction with *N*-phenylmaleimide

TABLE 1

Intramolecular photocyclisation reactions of phenyl vinyl bichromophoric systems

Compound	Position of vinyl attack on phenyl group	Product	$\Phi$ of intramolecular cyclisation
$\text{Ph}[\text{CH}_2]_3\text{CH}=\text{CH}_2$	2,6	(3)	0.11
	1,3	{ (6) (8)	0.02 0.023
<i>cis</i> - $\text{Ph}[\text{CH}_2]_3\text{CH}=\text{CHMe}^a$	1,3	{ (6) with <i>exo</i> -6-Me (8) with <i>exo</i> -7-Me	0.26
<i>trans</i> - $\text{Ph}[\text{CH}_2]_3\text{CH}=\text{CHMe}^a$	2,6	(3) with <i>endo</i> -7-Me	
(1a)	1,3	5,6- <i>exo</i>	0.006
	2,5	(11)	0.23
(1b)	1,3	{ (14) (15)	0.005 0.007
	2,4	(12)	0.05
(1c)	2,4	(16) <i>b</i>	<i>b</i>
$\text{PhO}\cdot\text{CH}_2\text{CH}_2\cdot\text{O}\cdot\text{CH}=\text{CH}_2$	1,4	(17)	<i>b</i>
(1d)	1,3	{ (7) (9)	0.03 0.02
	2,6	(4)	0.017

<sup>a</sup> Ref. 5. <sup>b</sup> Excessive polymeric deposits and very inefficient intramolecular cycloaddition prevented meaningful  $\Phi$  measurements.

indicating the absence of an intramolecular *ortho*-cycloadduct, we tentatively assigned the 1,4-cycloadduct structure (17) to the photoisomer of 2-phenoxyethyl vinyl ether; again it was impracticable to make meaningful quantum-yield determinations.

*Allyl Benzyl Ether* (1d).—In view of the foregoing results which demonstrate that the efficiency and selectivity of intramolecular cycloadditions of molecules of type (1) can be markedly affected by relative donor acceptor properties of the chromophores as well as the length of the intervening chain between them, it was considered desirable to investigate the photochemistry of allyl benzyl ether, in which the number of intervening units is three and the oxygen promotes neither chromophore to be an electron donor relative to the other. Irradiation of a 1% solution of (1d) in cyclohexane produced two reaction components in a ratio of 3:4 (g.l.c. elution sequence, Apiezon L/KOH columns) both of which had  $M^+$  148 m.u., consistent with isomers of the starting material. The product with shorter retention time was isolated in 85% purity (g.l.c.) by preparative g.l.c. and from the  $^1\text{H}$  n.m.r. spectrum was assigned the intramolecular cycloadduct structure (7) which reflects 1,3-attack of the vinyl on to the phenyl group. The second component, also with 85% purity (g.l.c.), was deduced to

be a 3:4 mixture of the two *meta*-adduct isomers (4) and (9) respectively. The assignments were made from detailed examination of the  $^1\text{H}$  n.m.r. spectrum and its comparison with those of the intramolecular cycloadducts of 5-phenylpent-1-ene together with consideration of molecular models.

The results from the present study are summarised in Table 1 along with those for the *cis*- and *trans*-6-phenylhex-2-enes.<sup>5</sup>

From none of the foregoing systems was evidence obtained for the presence of an *ortho*-cycloadduct but such products from intermolecular systems are very photolabile and as well as reverting to starting materials frequently cleave to yield derivatives of octa-1,3,5,7-tetraene. Such compounds have characteristic absorptions in the 280–320 nm range,<sup>16</sup> but none of the irradiated solutions examined in the present study had absorptions in this region and hence intramolecular *ortho*-cycloaddition was deduced not to have occurred.

*Spectroscopic Properties of (1a–d) and 5-Phenylhex-2-ene*.—The u.v. absorption spectra of 5-phenylhex-2-ene and (1a, b, and d) were recorded in cyclohexane solution and compared with those of toluene and *n*-pentylbenzene. In all cases the spectra were essentially identical showing only arene absorption in the 240–270 nm range with absorptivities of 210–250 mol<sup>-1</sup> l cm<sup>-1</sup>; the u.v. absorption spectra of (1c) and 2-phenoxyethyl vinyl ether were very similar to that of anisole. Thus, unlike 1,1-dicyano-2-methyl-4-phenylbut-1-ene,<sup>17</sup> for none of the bichromophoric molecules examined in the present study was evidence obtained for charge-transfer absorption. The radiation sources in all experiments were low-pressure mercury-arc lamps and hence in all cases the reactions proceeded by way of initial excitation of the phenyl group. The fluorescence spectra of 5-phenylpent-1-ene and (1a–d) were recorded as 0.000 4M solutions in 2-methylbutane at room temperature; the results are presented in Table 2. Broad longer-

TABLE 2

Fluorescence emission of phenyl-vinyl bichromophoric systems relative to *n*-pentylbenzene <sup>a</sup>

		$\lambda_{\text{max.}}$ /nm (emission)
5-Phenylpent-1-ene	0.08	284
(1a)	0.05	283
Ethyl phenethyl ether	0.85	283
(1b)	0.40	283
Ethyl 3-phenylpropyl ether	0.85	283
(1d)	0.15	283
Benzyl <i>n</i> -propyl ether	0.50	283.5
Benzyl vinyl ether	0.02	283
Benzyl ethyl ether	0.50	282.5
(1c)	0.3 <sup>b</sup>	

<sup>a</sup> Determined on a Perkin-Elmer MPF-2A fluorescence spectrophotometer at room temperature using comparative peak heights at  $\lambda_{\text{max.}}$  (emission) for 0.000 4M solutions in 2-methylbutane. <sup>b</sup> Relative to anisole using comparative peak heights at 297 nm.

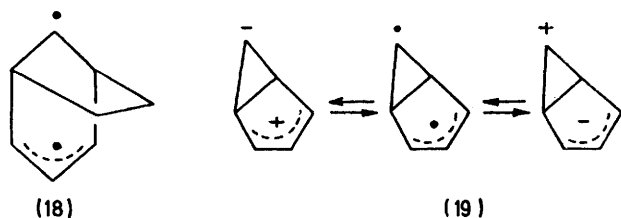
wavelength emission which could be attributed to that from an exciplex was not observed and similarly only arene fluorescence was observed in acetonitrile solutions with concentrations up to 0.5M in the bichromophoric molecule.<sup>10</sup>

## DISCUSSION

The principal observations reported in the Results section may be summarised as follows. Excitation of the phenyl group of the bichromophoric molecules of

type (1) resulted in intramolecular cycloaddition of the vinyl group on to the arene. The quantum efficiencies of the processes were very variable and with (1c) and 2-phenoxyethyl vinyl ether the major reaction involved polymerisation of the starting material. *meta*-Cycloaddition occurred with all but one compound (*i.e.* 2-phenoxyethyl vinyl ether) and depending upon the particular system, involved the 1,3-, 2,6-, and 2,4- but not the 3,5-positions of the arene. The normally disfavoured *para*-cycloaddition was observed as the major mode of reaction with two of the bichromophoric molecules. No ground-state interaction between the phenyl and vinyl chromophores was observed, but fluorescence spectroscopy provided evidence for varying degrees of interaction between the chromophores in the excited state.

Inspection of the data in Table 1 reveals interesting features of the present bichromophoric molecules. Thus whereas a decrease in reaction efficiency in going from three to four interposing units as in (1a) and (1b) may have been expected, the change in reaction mode is noteworthy and considered below in terms of conformations of the molecules. The three isomeric ethers (1a), (1c), and (1d) and 5-phenylpent-1-ene display significantly different photochemistries and illustrate that although the number of intervening units between the



reacting groups is important, as many workers have commented,<sup>18</sup> relative electron-donor-acceptor properties of the chromophores and the nature of the units in the chain joining them may also determine the efficiency of product formation, the extent of side reactions (principally polymerisation), the mode of reaction, and the preferred orientation of attack for simple phenyl-vinyl bichromophoric systems.

Two mechanisms have been proposed<sup>9,19</sup> and discussed<sup>2,9,12,20</sup> for the formation of *meta*-photocycloadducts from intermolecular systems and it is important to consider their involvement in the present reactions of bichromophoric systems and how such pathways may influence positions of attack and resultant substitution patterns of the intramolecular *meta*-adduct isomers. The two mechanisms involve (a) *meta*-ethylene addition to the arene to give (18) followed by formation of the vinylcyclopropane system<sup>9</sup> and (b) prior rearrangement of the arene to a species (19), termed prefulvene, followed by concerted attack of this on to the ethylene.<sup>19</sup>

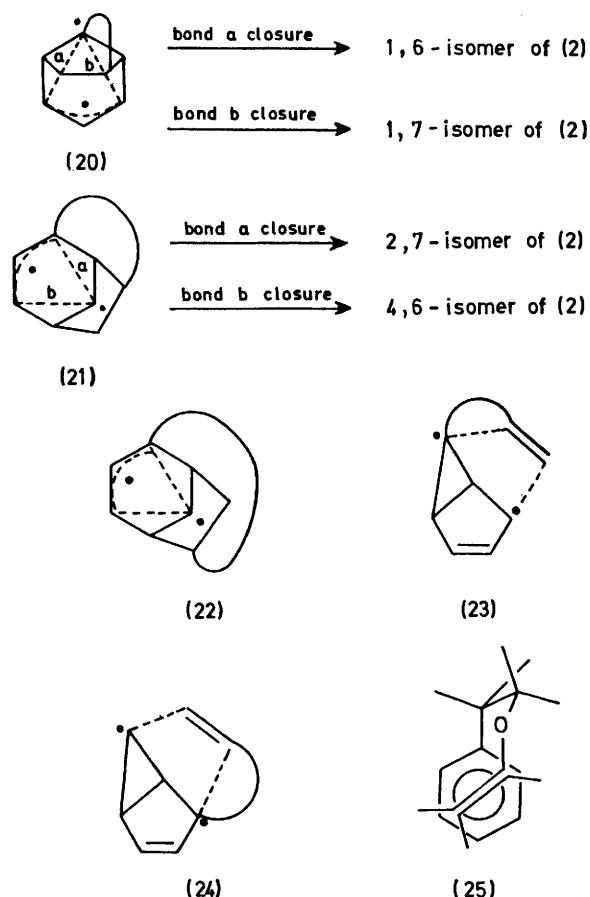
\* The different modes of closure to form the cyclopropane ring following 2,6-attack in these bichromophoric molecules can lead to two pairs, the 6- and 7-isomers, of enantiomers but, as noted in the text, formation of the 7-substituted product is greatly disfavoured.

Assuming that substituent stabilisation of radical centres, or polarised species, is important, then the former mechanism accounts for the exclusive 2,6-attack of certain ethylenes onto anisole and methylbenzenes which leads to 1-substituted isomers of (2),<sup>9</sup> whereas the latter pathways can rationalise the formation of the 3-, 5-, and 8-substituted isomers of (2) which are observed from other systems, and in some cases it is necessary to consider concurrent operation of both mechanisms.<sup>20-22</sup> From a consideration of these alternatives for the present systems, it can be appreciated that the former mechanism may operate in the 2,6-addition of (1c) and 5-phenylpent-1-ene leading to (4) and (3) respectively as shown in (20)\* and similarly may account for the 4,6-isomers (12) and (16) from (1b) and (1c) respectively involving 2,4-attack as depicted in (21).† In terms of the second mechanism and stabilisation of radical centres, then intermediates (23) and (24) are to be expected leading to the bridged 7,8- and 5,6-isomers of (2) but in contrast to some intermolecular systems,<sup>20,22,23</sup> products arising from formal 3,5-vinyl attack on the arene were not observed with the bichromophoric systems. The obvious reason for this is that the chain joining the chromophores in the present examples is too short to allow the vinyl group to 'sit' over or reach these positions; molecular models show that the products of such reaction which would have a bridge between the 3- and either of the *endo* 6- or 7-positions in (2) have little strain when there are more than three units in the intervening chain between the chromophores. Thus in simple terms of substituent stabilisation of radical or polarised intermediates a combination of the two pathways would account for the formation of the present intramolecular *meta*-cycloadducts but in such bichromophoric systems other features are also important and are considered below.

The *meta* cycloaddition by the first of the two mechanisms is considered to originate from an  $S_1$  arene- $S_0$  ethylene exciplex<sup>9</sup> and some evidence for this was provided by the studies of Morrison *et al.* of the intramolecular *meta*-cycloadditions of *cis*- and *trans*-6-phenylhex-2-enes,<sup>5</sup> and more recently by quenching of the addition reaction and exciplex emission in the 2,2-dimethyl-1,3-dioxole-benzene system.<sup>11</sup> The involvement of such excited-state complexes has also been postulated in the intermolecular *para*- and *ortho*-ethylene cycloadditions to benzene<sup>8,24</sup> which are formally 'forbidden' from orbital-symmetry analysis of the system in the absence of mixing with charge-transfer states.<sup>2,25</sup> 5-Phenylpent-1-ene and (1a) overall gave the most efficient photocycloaddition of those examined in the present study, and also, with the exception of benzyl vinyl ether, displayed the strongest quenching of the arene fluorescence. In the case of (1b), for which the total

† The alternative cyclopropane ring closure of (21) would yield an impossibly strained 2,7-structure for compounds having less than 5 intervening units between the chromophores, and the alternative mode of 2,4-attack to give intermediate (22) is considered to be very unlikely for the present number of intervening units between the chromophores.

quantum yield was only 0.06, the arene fluorescence was quenched by *ca.* 40–50% compared to that of the saturated ether and *n*-pentylbenzene. Thus reaction proceeding by interaction of the chromophores in the excited state and the formation of an exciplex, non-fluorescent under our conditions of study, is an attractive mechanistic pathway for the present reactions. Further, a comparison of the relative fluorescence intensities of 5-phenylpent-1-ene and allyl benzyl ether with that of *n*-pentylbenzene, alongside a similar examination of the efficiencies of the individual *meta*-cycloadditions observed for the two vinyl compounds, produces a connection between the mechanistic considerations for the *meta*-cycloaddition given above and the possible role of excited-state complexes in these reactions. Thus 2,6-



addition which is proposed to originate from an exciplex<sup>9</sup> has a quantum efficiency of 0.11 in the hydrocarbon but ether this mode of reaction was much less efficient with a quantum yield of formation of 0.02 whereas the products from formal 1,3-attack from both bichromophoric molecules have very similar quantum yields of formation and, as argued above, could have arisen by such intermediates as (23) and (24) in a mechanism which does not necessarily require interaction of the chromophores in the excited state. The relative arene fluorescence intensity of the vinyl hydrocarbon and ether is *ca.* 1:2 and this latter may well be reduced to the observed value by a contri-

bution from through-bond interaction of the phenyl group and ethereal oxygen (see below). The trend is thus that in the system in which the excited-state interaction was the weaker as deduced from fluorescence intensities, only the addition mode proposed to arise from an exciplex was significantly reduced, whereas the 1,3-process was essentially unaffected. However, why there should be this difference between the two systems is not immediately obvious but it may be a reflection of the conformations that the two molecules adopt affecting the extent of interaction in the excited state.

There has been some discussion in the recent literature concerning the features of bichromophoric molecules which promote or inhibit intramolecular arene fluorescence quenching and formation of fluorescent exciplexes.<sup>1a,b,26</sup> For systems in which the two chromophores are separated by only one methylene group, it would appear that quenching of the arene fluorescence seems likely to occur by interaction of the chromophores *via* the C-H bonds.<sup>26</sup> It may well be in the present systems that such a through-bond quenching mechanism involving the ethereal oxygen and phenyl groups can explain the reduced arene fluorescence intensity of benzyl *n*-propyl ether and benzyl ethyl ether compared to that of *n*-pentylbenzene, ethyl phenethyl ether, and ethyl 3-phenylpropyl ether. In cases where there is more than one intervening unit between the chromophores, then in order to understand the fluorescence quenching and exciplex emission phenomena, conformational aspects of the molecules must be examined. We were interested in this feature, which concerns the relative orientations that the two chromophores may adopt, in order to assess if this may explain why the normally highly disfavoured *para*-cycloaddition process was the preferred reaction with a reasonable quantum efficiency with phenethyl vinyl ether but not with 3-phenylpropyl vinyl ether, and also in an attempt to understand the positions of *meta*-attack of the vinyl chromophore on to the phenyl ring in the present series of bichromophoric molecules.

Examination of space-filling molecular models for compounds of type (1) and 5-phenylpent-1-ene revealed that some conformations were clearly more favoured than others and this leads to a preferential orientation of the two chromophores. For example with phenethyl vinyl ether, the conformation in which interaction of the two chromophores through space appears to be maximised and the ethane hydrogens are staggered is that depicted in (25) where the vinyl group is located between the 1,3- and 2,5-positions of the phenyl group with the bias towards the latter configuration. On the other hand, the preferred orientations in allyl benzyl ether placed the two chromophores in approximately 1,3- and 2,6-locations with the former being favoured but whereas a similar 1,3-orientation was satisfactory for 5-phenylpent-1-ene, the steric clash between the vinyl CH<sub>2</sub> and the  $\beta$ -methylene hydrogen in a 2,6-orientation was appreciable. Thus although there was some correlation between the observed positions of intramolecular

reaction of the vinyl and phenyl groups with preferred orientations deduced from space-filling molecular models for conformations in which interaction of the chromophores was judged to be maximised, the 'match' is far from exact and other, as yet not clearly defined, features of these bichromophoric compounds must be important in their intramolecular cyclisations. For example, it is difficult to understand why (1c) polymerises so readily and yields only minor amounts of the 2,4-attack product. In intermolecular benzene-ethylene photocycloadditions the relative electron-donor-acceptor properties of the addends are considered to have a significant directing effect on the mode of reaction<sup>12,27</sup> but in corresponding intramolecular systems, while such features must be taken into account, it seems more likely that the conformational aspects are more important.

It is evident from the present study that intramolecular cyclisation of bichromophoric phenyl vinyl systems is a significant route for deactivation of the photoexcited systems. The efficiency of this route is very variable and modes of reaction and positions of cycloaddition may well be dictated by preferred orientations of the chromophores in the excited state. The addition originating from an excited complex is an attractive mechanism but no emission from such species with phenyl-vinyl bichromophoric molecules has been observed and it may well be that the low efficiency 1,3-cycloadditions occur *via* prior arene rearrangement to a prefulvene species.

#### EXPERIMENTAL

The bichromophoric molecules as 1% solutions in cyclohexane (100 ml) under air in 30 × 2.5 cm diameter quartz tubes were subjected to radiation from Hanovia 15-W low-pressure mercury-arc lamps. The progress of the reaction was monitored by g.l.c. and polymeric deposits were periodically filtered off and removed from the tube walls. The standard work-up procedure simply involved removal of the cyclohexane solvent *in vacuo* at 40 °C and separation of the photo-products by preparative g.l.c. using columns packed with 9% Apiezon L/2% KOH supported on 60–80 mesh Universal B for the ethers, and 10% Carbowax 20M for 5-phenylpent-1-ene: these liquid phases were also used in the analytical g.l.c. The amounts of photoisomers obtained by this work-up were in the 10–150 mg range. The structures of the products were deduced by spectroscopic methods, principally <sup>1</sup>H n.m.r. spectroscopy, and this was greatly aided for the ethers by the addition of Eu(fod)<sub>3</sub>. As noted in the main text the spectroscopic features of such photoproducts are well documented and only those of particular relevance are given. Quantum yields were determined for 1% solutions of the bichromophoric molecules using a 5-W low-pressure mercury-arc lamp of calibrated output and ferrioxalate actinometry. The product concentrations were determined by g.l.c. Unless stated otherwise <sup>1</sup>H n.m.r. spectra were recorded at 100 MHz for [<sup>2</sup>H<sub>6</sub>]benzene solutions. I.r. spectra were recorded for liquid smears and u.v. spectra for cyclohexane solutions. The fluorescence spectra were of 0.000 4M solutions of the compounds (Table 2) in 2-methylbutane using 260-nm exciting radiation.

**Photoisomers of 5-Phenylpent-1-ene.**—The major photoisomer (3) of 5-phenylpent-1-ene (>95% purity, retention

time 0.85 that of starting material) had  $\delta$  (60 MHz; CDCl<sub>3</sub>) 5.6–5.8 (1 H, dd,  $J_{3,4}$  5.5,  $J_{3,2}$  2 Hz), 5.4–5.6 (1 H, dd and minor couplings,  $J_{4,3}$  5.5,  $J_{4,5}$  2,  $J_{4,2}$  1 Hz), 2.35–2.7br (2 H, m), 2.15–2.35br (1 H, s), 1.50–2.15 (8 H, broad resonance with minor splitting of *ca.* 2 Hz), and 0.7–1.0br (1 H, t,  $J$  *ca.* 4 Hz). This photoisomer was converted thermally into (5) (retention time 0.6 that of starting material) either at 150 °C or in the injection port at 300 °C of the preparative g.l.c. Compound (5) had  $\delta$  (60 MHz; CDCl<sub>3</sub>) 5.75 (2 H, s, very small splitting of *ca.* 0.5 Hz), 5.55–5.70 (1 H, dd + minor couplings,  $J$  6 and 2.5 Hz), 5.25 (1 H, d,  $J$  6 Hz), 2.5–2.7 (1 H, m) and 1.3–2.4 (9 H, unresolved multiplets) (Found: C, 90.05; H, 9.9. C<sub>11</sub>H<sub>14</sub> requires C, 90.4; H, 9.6%). The <sup>1</sup>H n.m.r. spectrum of (6) (retention time 0.53 that of starting material) (CDCl<sub>3</sub>) following subtraction of the spectrum of (5), the impurity, clearly revealed the AB quartet of the ethenyl protons at  $\delta$  5.6–5.75 (1 H, dd,  $J$  5.5 and 2 Hz), and 5.34–5.46 (1 H, dd and minor coupling,  $J$  5.5, 2, and 1 Hz); thus substitution must be at the 1- or 8-positions. The remainder of the <sup>1</sup>H n.m.r. spectrum between  $\delta$  1.0 and 2.5 integrated for 12 protons. The structurally significant part of the <sup>1</sup>H n.m.r. spectrum of (8) (retention time 0.67 that of starting material) (CDCl<sub>3</sub>) following subtraction of the spectrum of (5) was between  $\delta$  5.32 and 5.62 and comprised resonances  $\delta$  5.48–5.62 (1 H, dd,  $J$  5.5 and 2 Hz) and 5.32–5.46 (1 H, d,  $J$  5.5 Hz). Hence the  $J_{4,5}$  coupling was absent and C-5 must be substituted.

**Photoisomers of (1a).**—The major product (11) [retention time 1.6 that of (1a)] thermally and photochemically reverted to (1a). The isolated material contained 15% of (1a) but its <sup>1</sup>H n.m.r. spectrum could readily be obtained by subtraction and showed  $\delta$  5.5–5.85 (3 H, m,  $J$  5.5 and 1.0 Hz), 4.6br (1 H, s), 3.6–3.9 (2 H, m,  $J$  12 and 5 Hz), and 1.3–2.4 (6 H, complex m,  $J$  12 and 8 Hz). The coupling constants were determined for spectra recorded in the presence of Eu(fod)<sub>3</sub>. This photoisomer showed no reactivity to *N*-phenylmaleimide in refluxing diethyl ether solution for 6 h. The minor photoisomer [retention time 1.3 that of (1a)] from (1a) had  $\delta$  (60 MHz) at 5.4–5.6br (1 H, d,  $J$  5.5 Hz), 5.1–5.35 (1 H, d,  $J$  5.5 Hz), 3.4–4.3 (4 H, overlapping multiplets), and 1.55–2.2 (6 H, overlapping multiplets).

**Photoisomers of (1b).**—Irradiation of (1b) in cyclohexane produced three photoisomers of (1b) and trace amounts of dicyclohexyl ether which was identified from its i.r., <sup>1</sup>H n.m.r., and mass spectra.<sup>28</sup> The major photoisomer (12) [retention time 2.3 that of (1b)] was separated with 99% purity (g.l.c.),  $M^+$  162.102 9, and had  $\delta$  5.22 (1 H, t,  $J$  2 Hz), 4.32–4.60 (1 H, ddd,  $J$  9.5, 8.5, and 6 Hz), 3.16–3.66 (2 H, complex m), 2.85 (1 H, t,  $J$  6 Hz), and 1.1–2.4 (9 H, unresolved multiplets). Assignments were made following spin-decoupling and Eu(fod)<sub>3</sub> addition experiments. The structurally significant part of the <sup>1</sup>H n.m.r. spectrum of the minor isomer (14) [retention time 1.25 that of (1b)] comprised the ethenyl proton resonances in the  $\delta$  5.0–5.55 region:  $\delta$  5.07 (1 H, d,  $J$  5.5 Hz) and 5.50 (1 H, d with minor splitting,  $J$  5.5 Hz); hence C-5 must be substituted. The second minor isomer (15) [retention time 1.6 that of (1b)] had  $\delta$  5.4–5.52 (1 H, dd,  $J$  6 and 2.5 Hz), 5.15–5.3 (1 H, dm,  $J$  6 Hz), 4.25br (1 H, s), 3.7–3.85br (2 H, t,  $J$  4 Hz), and 1.5–3.4 (9 H, overlapping m with brs at  $\delta$  3.85).

**Photoisomer of (1c).**—Much polymer was formed on irradiation of a 1% cyclohexane solution of (1c). The photoisomer (16) [retention time 1.3 that of (1c)] isolated by the above procedure contained 40% of (1c) but again

its  $^1\text{H}$  n.m.r. spectrum was obtained by subtraction. The i.r. spectrum of (16) had a strong absorption at  $1680\text{ cm}^{-1}$  indicative of an enol ether and it showed  $\delta$  5.52 (1 H, t,  $J$  2 Hz), 3.4–4.0 (3 H, overlapping m), 3.0–3.15 (1 H, m), and 0.9–2.5 (7 H, overlapping multiplets).

**Photoproducts of 2-Phenoxyethyl Vinyl Ether.**—As already noted only very low yields of volatile products were obtained from irradiation of this diether in cyclohexane. Dicyclohexyl ether (retention time 1.6 that of starting material) was identified by m.s.-g.l.c. A second product (retention time 1.8 that of starting material) had no distinct parent ion but abundant ions were observed at  $m/e$  117, 99, and 83 and was judged to be derived from the solvent. The isomer (17) (retention time 1.4 that of starting material) constituted <30% of the product mixture and could only be isolated in amounts required for spectroscopic analysis as a 40% mixture with the starting material to which it readily reverted both under the conditions of its formation and thermally. No reaction was observed on refluxing the mixture with *N*-phenylmaleimide in ether for 10 h. Taking into account the impurities the  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) showed the presence of four ethenyl proton resonances in the  $\delta$  5.5–6.1 region (m), the methine  $\alpha$  to oxygen at  $\delta$  4.63 (d,  $J$  2.5 Hz), and the remaining 7 proton resonances spread over  $\delta$  3.4–4.0 (4 H) and 1.5–2.4 (3 H).

**Photoisomers of (1d).**—The  $^1\text{H}$  n.m.r. spectrum (60 MHz;  $\text{CDCl}_3$ ) of (7) [retention time 1.4 that of (1d)] had  $\delta$  5.55–5.75 (1 H, dd,  $J_{3,4}$  5.5,  $J_{3,2}$  2 Hz), 5.35–5.55 (1 H, dd + further splitting,  $J_{4,3}$  5.5,  $J_{4,5}$  2 Hz), 3.55–4.0 (4 H, m), 3.15–3.50 (1 H, m), 2.4 (1 H, t,  $J_{1,5} = J_{1,2} = 7$  Hz), and 1.6–2.2 (4 H, m,  $J_{2,1}$  7,  $J_{2,3}$  2 Hz). The  $^1\text{H}$  n.m.r. spectrum of the second component [retention time 1.6 that of (1d)] showed an overall ratio of ethenyl protons to protons on saturated C atoms of 2 : 10 but from the spectrum, particularly the  $\delta$  5–6 region, was clearly a mixture and by analysis of this region and comparison of the spectrum with those of other *meta*-cycloadducts was deduced to be comprised of (9) and (4) in a 4 : 3 ratio. Thus 3-H and 4-H of (9) appeared at  $\delta$  5.6–5.7 (dd,  $J_{3,4}$  5.5,  $J_{3,2}$  2 Hz) and 5.35–5.45 (d,  $J_{3,4}$  5.5 Hz), respectively; hence 5-H was absent, whereas the 3-H and 4-H resonances of (4) were at  $\delta$  5.74–5.82 and 5.55–5.65, respectively, and had 5.5 and 2.0 Hz couplings on each; hence for (4) 5-H was present. The  $^1\text{H}$  n.m.r. spectrum of the mixture of (4) and (9) had  $\delta$  5.35–5.85 (2 H), 3.4–4.2 (3 H, m), 2.8–3.4 (1 H, m), 2.2–2.7br (2 H, m), 1.6–2.1 (3 H, m), and 1.2–1.5 (1 H, m).

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