Photocycloaddition Reactions of Phenyl–Vinyl Bichromophoric Systems

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Summary The efficiency and mode of intramolecular photocycloaddition of the bichromophoric molecules $Ph[CH_2]_mO[CH_2]_nCH{=}CH_2$ are shown to depend on the values of *m* and *n* and on the overall chain length; the importance of ethereal oxygen at the various positions in the chain is demonstrated by comparison of the results with those obtained from hydrocarbon systems.

Intramolecular excited state interactions and reactions of bichromophoric molecules have attracted considerable interest in recent years,[1] but although knowledge of intermolecular benzene–ethylene photoaddition reactions is extensive,[2] examples of the corresponding intramolecular process are limited to three reported cases.[3,4,5] We now report on the photochemistry of compounds of the type $Ph[CH_2]_mO[CH_2]_nCH{=}CH_2$ and note that both the mode and efficiency of reaction is markedly dependent on the values of *m* and *n* and the relative electron donor–acceptor properties of the two chromophores.

The bichromophoric molecules were irradiated (254 nm) as 1% solutions in cyclohexane, under air (degassing under nitrogen having little effect), at 20 °C. The products were concentrated by solvent removal and separated by preparative g.l.c. (Carbowax 20M or Apiezon L). The assignment of structures to the intramolecular cycloadducts was essentially based on their n.m.r. spectra, the interpretation of which was greatly aided by data obtained in the presence of a europium shift reagent. Other spectroscopic properties, thermal labilities, and inertness to common dienophiles supported the assignments. The results are summarised in the Table which also includes our findings with 5-phenylpent-1-ene (**2**) and those of Morrison *et al.* for the 6-phenylhex-2-enes (**3**) and (**4**).[3]

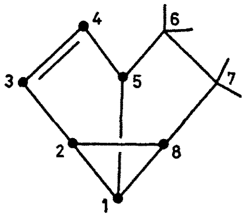
Several aspects of the data are noteworthy. Although (**2**) yields only the same type of product as the 6-phenylhex-2-enes, the preferred mode of its *meta* intramolecular attack is that of the *trans* isomer (**4**) rather than that of the *cis* ethylene (**3**) which did not undergo 2,6-attack. Ethereal oxygen at any position in the connecting chain between the phenyl and vinyl units obviously and markedly affects the efficiency and mode of reaction between the chromophores. Whereas allyl benzyl ether (**5**) yields products resulting from the same mode of addition as the hydrocarbon (**2**), irradiation of (**6**), in which the phenyl group is an electron donor relative to the vinyl group, produced large amounts of polymer and a very slow cyclisation reaction to yield but one isomer of (**1**) resulting from 2,4-attack; on the other hand the isomer (**7**), where now the vinyl group is comparatively the electron donor, gave little polymer and a reasonably efficient formation of the *para* cycloadduct and only one (5,6 *exo*) of the two possible isomers from 1,3-attack. The importance of the length of the intervening

Table. Intramolecular photocyclisation of phenyl-vinyl bichromophoric compounds

Compound	Orientation of vinyl attack (adduct type[a])	Substitution of (**1**) and stereochemistry	Quantum yield of adduct formation[b]
$Ph[CH_2]_3CH{=}CH_2$ (**2**)	2,6-(*meta*)	1,6 *exo*	0·11
	1,3-(*meta*)	5,6 *exo*	0·023
		8,7 *exo*	0·018
cis-$Ph[CH_2]_3CH{=}CHMe$[3] (**3**)	1,3-(*meta*)	5,6 *exo*	0·26
		8,7 *exo*	—
trans-$Ph[CH_2]_3CH{=}CHMe$[3] (**4**)	2,6-(*meta*)	1,6 *exo*	
$PhCH_2OCH_2CH{=}CH_2$ (**5**)	2,6-(*meta*)	1,6 *exo*	0·017
	1,3-(*meta*)	5,6 *exo*	0·022
		8,7 *exo*	0·03
$PhO[CH_2]_2CH{=}CH_2$ (**6**)	2,4-(*meta*)	4,6 *endo*[e]	—[c]
$Ph[CH_2]_2OCH{=}CH_2$[5] (**7**)	1,3-(*meta*)	5,6 *exo*	0·006
	2,5-(*para*)	—	0·23
$Ph[CH_2]_3OCH{=}CH_2$[d] (**8**)	1,3-(*meta*)	5,6 *exo*[f]	0·003
		8,7 *exo*[f]	0·007
	2,4-(*meta*)	4,6 *endo*[e]	0·05
$PhO[CH_2]_2OCH{=}CH_2$[d] (**9**)	1,4-(*para*)	—	—[c]
$PhCH_2OCH{=}CH_2$	No cycloaddition[g]		

[a] The nomenclature of *meta etc.* to describe the cycloaddition mode is consistent with that in D. Bryce-Smith, W. M. Dadson, A. Gilbert, B. H. Orger, and H. M. Tyrell, *Tetrahedron Letters*, 1978, 1093. [b] In all cases the ϕ for disappearance of starting material was appreciably greater than that of adduct formation. The difference between the two values was at a maximum for (**9**) where the ratio was *ca.* 20:1. [c] Excessive polymer deposits and very inefficient intramolecular cycloaddition reaction rendered ϕ measurements impractical. [d] Dicyclohexyl ether also formed. [e] The 2,7 isomer of (**1**) from the 2,4-mode of attack is, from molecular models, extremely strained and was not observed. [f] The stereochemical assignment is tentative. [g] In agreement with J. T. Pinhey and K. Schaffner, *Austral. J. Chem.*, 1968, **21**, 2265, we have found that irradiation of benzyl vinyl ether yields β-phenylpropionaldehyde almost quantitatively. Allyl phenyl ether is well-known to give the products of the Claisen rearrangement when irradiated (see H. R. Waespe, H. Heimgartner, H. Schmid, H. J. Hansen, H. Paul, and H. P. Fischer, *Helv. Chim. Acta.*, 1978, **61**, 401.)

chain between the chromophores is well demonstrated in the present system by the results from the irradiation of (**7**) and (**8**), but again with chains of similar length the effect of the relative electron donor–acceptor properties of the chromophores is emphasised by the contrasting behaviours of (**8**) and (**9**).



(1)

● = benzene derived C-atoms.

Compounds (**2**)—(**6**) react in an analogous manner to their intermolecular counterparts[2,6] although in the former compounds steric constraints may dictate positions of attack and the stereochemistry of the adducts. Similar comparison for (**7**)—(**9**) is, however, less favourable since irradiation of ethyl vinyl ether with benzene yields *ortho* and *meta* cycloadducts with a ϕ ratio of 4:1 respectively,[7] but in the present systems no evidence for the formation of an *ortho* intramolecular adduct was obtained,[8] and whereas anisole and ethyl vinyl ether yield exclusively 2,6-cycloaddition[7] (**9**) gave only the *para* cycloadduct and much polymer.

The arene fluorescence in the intramolecular systems is quenched by the vinyl chromophore with an efficiency which, as may be expected, is variable but no longer-wavelength broad emission was observed from any system and intramolecular exciplex involvement in the photoprocesses remains an open question. No evidence was obtained for charge-transfer absorption resulting from interaction of the ground-state chromophores.[9]

It is evident from the present study that the number and type of units which separate the chromophores and the latter's relative electron donor–acceptor properties are important features which together or separately may determine the efficiency of product formation, the extent of side reactions (principally polymerisation), the mode of attack and, for *meta* cyclisation processes, the preferred orientation of substitution for simple phenyl–vinyl bichromophoric systems. Such aspects with similar systems but involving connecting units other than alkanes and ethers are currently under investigation.

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[1] See for example G. S. Beddard, R. S. Davidson, and T. D. Whelan, *Chem. Phys. Letters*, 1978, **56**, 54; J. C. de Schryver, N. Boens, and J. Put, *Adv. Photochem.*, 1977, **10**, 359; R. S. Davidson in 'Molecular Association,' Vol. 1, ed. R. Foster, Academic Press, New York, 1975, p. 216, and references therein.

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

[3] W. I. Ferree, J. B. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **43**, 5502.

[4] A. S. Kushner, *Tetrahedron Letters*, 1971, 3275.

[5] A. Gilbert and G. Taylor, *J.C.S. Chem. Comm.*, 1978, 129.

[6] R. Srinivasan, *J. Amer. Chem. Soc.*, 1971, **93**, 3555; J. Cornelisse, V. Y. Merritt, and R. Srinivasan, *ibid.*, 1973, **95**, 6197; J. A. Ors and R. Srinivasan, *J. Org. Chem.*, 1977, **42**, 1321.

[7] A. Gilbert and G. Taylor, *J.C.S. Chem. Comm.*, 1977, 242.

[8] See for example J. Atkinson, D. Ayer, G. Buchi, and E. Robb, *J. Amer. Chem. Soc.*, 1963, **85**, 2257.

[9] Evidence for charge-transfer absorption has, however, been obtained for the bichromophoric molecule 1,1-dicyano-2-methyl-4-phenylbut-1-ene; A. B. D. Ferreira, D. Sadler, and K. Salisbury, personal communication.