The Influence of Pressure on Arene–Ethene Photocycloaddition Reactions

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Pressures of as little as 500 bar have been shown to exert a substantial effect upon rates and product ratios of *ortho* and *meta* photocycloadditions of ethenes to the benzene ring. In all cases, rates are enhanced by pressure and calculated 'pseudo-activation volumes' for both modes of addition appear to be of similar magnitude to those of thermal cycloaddition processes. The pressure-induced discrimination between isomeric *meta* cycloadducts from the ethyl vinyl ether–benzene system is rationalised in terms of the mechanism involving partial charge separation in the S_1 arene and is backed up by calculated molar volumes of the adducts. Similar results are observed for the intramolecular photocycloaddition reactions of arene–ethene non-conjugated bichromophores.

In recent years the technique of high pressure as a useful variant in organic synthesis has been the subject of much interest and, as a result, a considerable number of reports have been published concerned with the effect of pressure on thermal processes, especially cycloaddition reactions.[1–3] In many systems, product yields are markedly increased and greater selectivity may be induced in isomer formation. In marked contrast, the influence of pressure on photoinduced processes has received only scant attention and in particular, surprisingly little interest has been shown in the vast range of photocycloaddition processes despite the early prediction that the effects of pressure on such reactions 'should be much more prominent and distinctive, in favourable cases, than can normally be expected for reactions in the ground state'.[5] The application of pressure to photochemical processes does, however, present a number of experimental challenges and as noted by Asano and Le Noble 'the interpretation of observed effects is not always straightforward'.[3] Absolute rate constants for chemical conversions of excited states under high pressure are, in general, not known, and in exceedingly fast reactions (*i.e.* when barriers are very low) the formalism of the absolute rate theory may not be applicable. Thus, although pressure effects may be observed, and may even be comparable to those reported for slower reactions, they cannot necessarily be equated to differences in partial molar volumes between the reactants and the activated complex.

It may be for these reasons that attempts reported over the years to induce greater selectivity into photochemical processes by the application of external factors have largely involved incorporation of the reactant(s) in ordered matrices such as crystal lattices,[6] cyclodextrin[7] and zeolite[8] cavities, crown ethers,[9] cryptands,[10] micelles[11] and microemulsions.[12] The effects on photoreactivity of compounds supported on silica and alumina,[13] and complexed with metal ions[14] have also been investigated.

The factors which may influence the inter- and intramolecular *ortho* (1,2-) and *meta* (1,3-) photocycloaddition of ethenes to the benzene ring have been of concern to several groups of workers for some years.[15,16] These processes are mechanistically intriguing and have been shown to have considerable synthetic potential.[16] The reaction mode and the regio- and stereochemistries of the cycloadditions can be selectively directed by the electronic characteristics and steric effects of the addend substituents. Mechanistic pathways to accommodate the experimental observations have been proposed[16] and these have received support from theoretical studies.[17] The influences and directing effects of the addend substituents, and the effect of linking the reactants by a propane chain (*i.e.* the photochemistry of 5-phenylpent-1-ene derivatives) may be expected to become more pronounced with increase in solution pressure. We have investigated the influence of pressure on the photocycloadditions of ethenes to the benzene ring not only to determine its potential, as in thermal processes, to increase reaction selectivity and efficiency, but also to assess whether the results would verify the interpretation of the influences of addend substituents and so provide a further insight into the factors which control the photoprocesses.

Results and Discussion

The systems chosen to assess the effect of pressure on the 1,2- (*ortho*) and 1,3- (*meta*) photocycloadditions to the benzene ring were selected from those we have previously studied at 1 bar.† The present experiments involved 254 nm irradiation at 1 bar and up to 1 kbar pressure of *ca.* 1 cm^3 solutions of the addends in acetonitrile or methylcyclohexane solution. Conversions of the arenes were to less than 10% in order to prevent the occurrence of secondary photoreactions and the adducts were thermally stable under their conditions of formation. Chemical yields from all the arene–ethene systems studied are estimated to be greater than 80%. The adducts were identified by comparison of their chromatographic behaviour and mass spectral fragmentation patterns with those of the photoadducts of proven structures.

1,2- (ortho) *Photocycloaddition.*—Arene–ethene pairs which have an obvious electron donor-electron acceptor relationship preferentially undergo 1,2-photocycloaddition and the process is accelerated by an increase in the polarity of the solvent.[18] At 1 bar, this mode of reaction is exclusive for the benzene–acrylonitrile system in acetonitrile solution giving a *ca.* 2.5:1 ratio of the *endo* and *exo* isomers of 7-cyanobicyclo[4.2.0]octa-2,4-diene (**1**), respectively, with a quantum yield of 0.09.[19] Increase in the pressure of the solution to 700 bar increased the rate of total adduct formation by 6.5-fold with a unity ratio of the stereoisomers. This latter datum is surprising since it appears that the formation of the 7-*exo* isomer is subject to greater acceleration than that of the spatially more compact *endo* isomer. However, we have noted that the two isomers of **1** are very readily converted thermally and the ratios observed may not truly reflect the relative rates of formation.[20] A measure of the influence of pressure on a reaction is given by the volume of activation ($\Delta V^{\ddagger}$) which is the difference in partial molar

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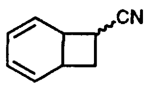
† 1 Bar ≡ 10^5 Pa.



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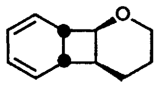

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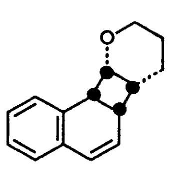

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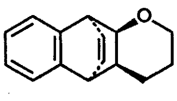

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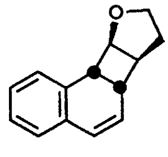

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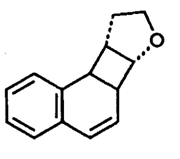

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Table 1 Effect of pressure and solvent on the rate of 1,2-photocycloaddition of 2,3-dihydropyran to benzene and naphthalene

	Solvent			
	Methylcyclohexane		Acetonitrile	
Arene; (adduct)	1 bar	500 bar	1 bar	500 bar
Benzene; (**2**)	1.00	1.75[a]	2.40[a]	0.60[a]
Naphthalene; (**3**)	1.00[c]	2.60[b,d]	1.40[b,c]	2.00[b,e]

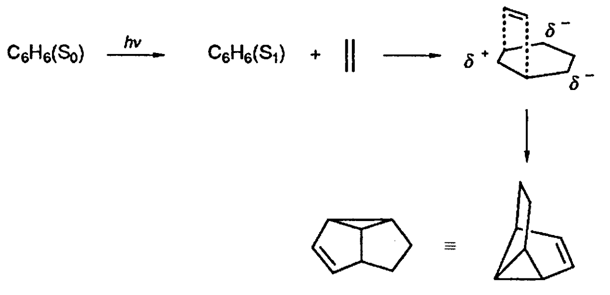
[a] Values normalised to adduct **2** formation in methylcyclohexane at 1 bar. [b] Values normalised to adduct **3** formation in methylcyclohexane at 1 bar. [c] No secondary photoproduct **4** detected. [d] Contains *ca.* 25% of the secondary photoproduct **4**.[23] [e] Contains *ca.* 20% of the secondary photoproduct **4**.

volume between the transition state and the reactants and is obtained experimentally from the gradient of the slope as $P \rightarrow 0$ of the plot of ln k *vs.* pressure. The complications referred to above of studying photochemical reactions under pressure do not play a significant part when only product distributions are considered,[4] but do affect the measurement of activation volumes for photoinduced processes and it seems appropriate to refer to such derived values as 'pseudo-activation volumes' *i.e.* a single number which offers a measure of the effect of pressure on a photochemical reaction, as suggested by Asano and Le Noble.[3] The 'pseudo-activation volume' of the present 1,2-photocycloaddition obtained from studies over the pressure range 1–700 bar was -31 cm^3 mol^{-1} in acetonitrile. The reaction was extremely slow in methylcyclohexane and the results obtained from prolonged irradiations lacked the necessary reproducibility. The value from acetonitrile solutions, however, is in good agreement with that expected from order of magnitude estimates based on a polar mechanism in which there is partial formation of two C–C σ-bonds in the intermediate. Although the 'pseudo activation volume' may not necessarily be directly comparable with the volumes of activation for thermal processes such as the Diels–Alder cycloaddition ($\Delta V^{\ddagger} = -25$ to -45 cm^3 mol^{-1}) and thermal ($2\pi + 2\pi$) cycloadditions which proceed by way of polar intermediates ($\Delta V^{\ddagger} = -35$ to -50 cm^3 mol^{-1}),[2,3,21] it does provide evidence of a similar 'pressure advantage'.

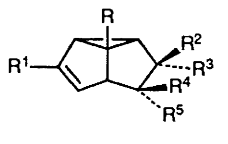
As shown by the data in Table 1, appreciable enhancement of the reaction rate for 1,2-photocycloaddition also occurred with an increase in pressure for the reverse-demand addend pairs benzene–2,3-dihydropyran[22] and naphthalene–2,3-dihydropyran[23] in methylcyclohexane solution. However, while the increase in the rate of formation at 1 bar of the two 1,2-cycloadducts **2** and **3** with increase in solvent polarity is expected, the effect of pressure on these photocycloadditions in acetonitrile is most surprising. Since the system and the nature of the reaction are unchanged when a more polar medium is employed, the explanation for the reduction in the yield of **2** and the smaller increase in the rate of formation of **3** on change of the solvent from methylcyclohexane to acetonitrile at the higher pressure, must lie in the electrostrictive term of the activation volume. The influence of the electric field caused by the participation of a dipolar intermediate in the mechanism, which induces reorganisation of the surrounding solvent molecules, extends to a greater distance from the charge centre in the less polar medium. This feature gives rise to a large (negative) contribution to the activation volume and hence a larger effect of pressure in the less polar medium (*i.e.* methylcyclohexane). Nonetheless, it is remarkable that in a polar solvent at 500 bar the yield of **2** is only 60% of that from methylcyclohexane at 1 bar.

Increase in pressure similarly accelerates the cycloaddition of 2,3-dihydrofuran to the 1,2-positions of naphthalene[23] in methylcyclohexane solution but in this system, interesting changes in adduct isomer ratios are also induced. Thus, while the overall rate of reaction is increased 3.5-fold from 1–700 bar, the ratio of the *exo* 'head-to-head' adduct **5** to the *endo* 'head-to-tail' isomer **6** changes from respective values of 1 : 7 to 1 : 2 by this increase in pressure. Furthermore, this increase in the overall yield results from a 2-fold increase in the rate of formation of the *endo* isomer **6** but an 8-fold increase in the less sterically compact *exo* stereoisomer **5**. Such a dramatic effect on the formation of **5** may reflect a pressure assisted stabilisation of the partial charges on the 1- and 2-positions of the S_1 excited naphthalene intensifying and increasing the importance of the 1,2- 2′,3′-interaction of the arene and the enol ether.

1,3-(meta) *Photocycloaddition.*—The regio- and stereochemistries of *meta* photocycloaddition of ethenes to the benzene ring are controlled by the substituents on the arene and ethene, respectively.[16] Such direction of the reaction can be understood in terms of the mechanism outlined in Scheme 1 involving polarisation of the C_6 ring on approach of the ethene to the arene.[24] The preferred *endo* addition of cycloalkenes is then accounted for by an intermolecular bonding interaction between the α-hydrogens of the ethene and the developing negative charge on the S_1 arene.[25] We observed, however, only a minor increase (*ca.* 5%) in the *endo*:*exo* ratio of *meta* photocycloaddition of *cis* cyclooctene to benzene on increase of



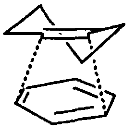
Scheme 1



7 R = R^1 = R^2 = R^5 = H, R^3-R^4 = -(CH$_2$)$_6$-
8 R = R^1 = R^3 = R^4 = H, R^2-R^5 = -(CH$_2$)$_6$-
9 R = CMe$_3$, R^1 = R^2 = R^5 = H, R^3-R^4 = -(CH$_2$)$_6$-
10 R = R^2 = R^5 = H, R^1 = CMe$_3$, R^3-R^4 = -(CH$_2$)$_6$-
13 R = R^1 = R^2 = R^4 = R^5 = H, R^3 = OEt
14 R = R^1 = R^2 = R^3 = R^5 = H, R^4 = OEt
15 R = R^1 = R^2 = R^3 = R^4 = H, R^5 = OEt

pressure to 700 bar: this may reflect the fact that, for such a bulky ethene, there is little overall difference in the volume requirements of the two adduct stereoisomers **7** and **8**. The rate of this *meta* cycloaddition is, however, significantly accelerated by pressure and this corresponds to a pseudo volume of activation, $\Delta V^{\ddagger}$ of *ca.* $-30\ \mathrm{cm^3\ mol^{-1}}$ which, as noted above, is of the same order as those for thermal cycloaddition processes. Similarly, although the overall rate of *meta* cycloaddition is increased for the *tert*-butylbenzene–*cis*-cyclooctene system,[25] increase in pressure does not discriminate between the 2,6-*endo* and 3,5-*endo* orientations of *meta* photocycloaddition which give the two regioisomers **9** and **10**, respectively. However, for the photoaddition of toluene to this ethene, discrimination between these two orientations of attack does occur to some extent. Thus, the *ca.* 25% increase in the overall rate by increase in pressure from 1 bar to 1 kbar largely results from a 50% increase in the efficiency of the 3,5-attack. The origin of the decrease in the ratio of the products from the 2,6- and 3,5-orientations of the addends, contrasts with the same effect observed at 1 bar resulting from an increase in the steric bulk of the alkyl substituent on the benzene ring: in these experiments, the efficiency of the 3,5-cycloaddition is essentially constant while that of the 2,6-declines markedly.[25,26]

We have recently attributed the anomalously low efficiency of the *endo meta* photocycloaddition of cyclohexene to benzene to steric interactions between the β-CH_2 of the cycloalkene and the arene as shown in **11**.[25] Such effects are not present in an *exo* approach of the addends and the *exo meta* adduct from cyclohexene is formed with similar efficiency to that of the corresponding stereoisomer from, for example, cyclopentene. It was of interest to assess the effect of pressure on the cyclohexene system since increase of this parameter is known to overcome steric barriers in thermal processes.[1–3] Satisfyingly, at 1 kbar pressure, not only is there an almost two-fold increase in the total adduct formation compared to 1 bar, but also the 2:1 ratio of the *endo* to *exo* stereoisomers of the *meta* cycloadduct at the lower pressure is increased to 3.2:1, respectively. Thus, there is a greater effect on the acceleration of the sterically hindered *endo* than on the spatially less compact *exo meta* photoadduct formation.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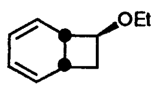

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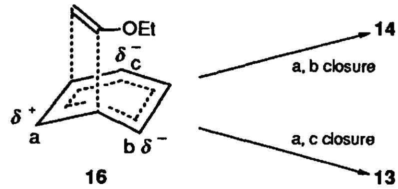
The photoaddition of vinyl ethers[22] and dioxoles[27] to benzene is more complex than the reactions considered above. At 1 bar pressure, the *ortho* and *meta* photocycloadditions occur with similar efficiencies and in the latter mode of reaction the ratio of stereoisomers reflects the effectiveness of the repulsive and attractive interactions between the oxygen lone pairs on the enol ether and the developing negative and positive charges, respectively, in the polarised S_1 arene. Such systems, therefore, provide the opportunity to assess competitive pressure effects on reaction modes and on the stereochemistry of the cycloaddition processes. The effect of pressure on these features was studied with the ethyl vinyl ether–benzene system.[22] At 1 bar pressure, the four major products (>95% of the reaction mixture) are the *exo* 7-ethoxy *ortho* adduct (**12**), the *endo* 7-ethoxy *meta* adduct (**13**), the *endo* 6-ethoxy *meta* adduct (**14**), and the *exo* 6-ethoxy *meta* adduct (**15**): these are formed in a respective ratio of 5:5:2:1. The effect of pressure (700 bar) on this system is dramatic. There is a decrease in the overall rate of photocycloaddition by *ca.* 30% but the effects on the individual isomers differ markedly. Thus, while the yield of the *ortho* adduct **12** drops over four-fold and those of the *meta* cycloadducts **14** and **15** by some 50%, formation of the *endo* 7-ethoxy *meta* adduct (**13**) is increased by 25%. The marked reduction in the formation of the *exo ortho* cycloadduct is unexpected, particularly in view of the appreciable increase observed for both the *endo* and *exo ortho* adducts from the benzene–acrylonitrile system. However, and most significantly, the ratio of the two isomers **13** and **14** resulting from *endo meta* photocycloaddition, changes from 1:2.5 at 1 bar to 1:6 at 700 bar pressure. As shown in Scheme 2, these isomers result from the two directions of intramolecular cyclisation in the reaction intermediate **16** to give the cyclopropane ring in the adducts. Such isomer formation will arise whether the cyclopropane ring formation occurs simultaneously with, or subsequent to, the intermolecular bonding between the benzene and the ethene. The preference for the *endo* 7-ethoxy isomer formation is accounted for by a repulsive interaction between the oxygen lone pair and the developing negative charge in the S_1 benzene causing asymmetric distortion of the C_6 ring which effectively brings together carbon atoms a and b, and hence facilitates the cyclisation between these positions. At 1 bar pressure for the ethyl vinyl ether–benzene system this effect does lead to a degree of selectivity, but where the *endo* substituent is chlorine, as for *trans* dichloroethene as the addend, then the distortion must be severe since the 7-*endo* adduct isomer is formed exclusively.[28] In the present system the marked increase in the discrimination between the two *endo meta* isomers **13** and **14** on increase in pressure indicates an increase in the asymmetric distortion of the C_6 ring. Such a pressure effect would be operational during the approach of the addends but could not be evident after bonding and formation of a (polarised) bicyclo[3.2.1]octenyl diradical intermediate. Thus, the present results are more consistent with the direction of cyclopropane ring formation being controlled prior to, rather than subsequently to, bond formation between the ethene and the benzene ring. Furthermore, it is relevant to note that our volume calculations from molecular mechanics (MM2) using the QCPE program number 554 GEPOL/87, show that of the four possible *meta* cycloadducts from benzene and ethyl vinyl ether, the *endo* 7-ethoxy isomer (**13**) has the lowest volume.



Scheme 2

A similar increase in the proportion of the *endo* 7-ethoxy *meta* adduct isomer at the expense of the *endo* 6-isomer on increase in pressure is also noted for the adducts from the irradiation of the anisole–ethyl vinyl ether system, but in this case the *exo* 6-ethoxy isomer is the major adduct at both 1 and 700 bar pressure.

Finally, we examined the influence of pressure on the photocycloaddition reactions of the arene–ethene non-conjugated bichromophores, 5-phenylpent-1-ene,[29] 5-(2′-methylphenyl)-pent-1-ene,[29] phenethyl vinyl ether,[30] 1-(4′-but-1′-enyl)-indan,[31] and 2-(1′-naphthyl) vinyl ether.[23] In all cases, the formation of the adducts obtained at 1 bar pressure was appreciably accelerated by increase in pressure (*e.g.* four-fold for the indan–ethene bichromophore at 1.2 kbar). However, only for 5-phenylpent-1-ene was any appreciable discrimination between intramolecular adduct formation observed at the higher pressure. For this bichromophore, the sole product from the 1,3-addition had the 5,6-bridged dihydrosemibullvalene skeleton: this is spatially more compact than the alternative product, the 7,8-bridged isomer which is formed in approximately equal amounts at 1 bar pressure.

Experimental

High Pressure Photochemistry.—The high pressure photochemical cell consisted of a sample chamber of 0.5 cm diameter (*ca.* 1 cm^3 capacity) fitted with a 0.5 cm diameter sapphire window at one end. The sample to be irradiated was sealed under butane gas and a piston with a Bridgeman-type seal was driven into the sample chamber by a screw attached to a pressure transducer. The transducer was calibrated to the pressure inside the chamber (1 mV $\equiv$ 0.2080 kbar). The apparatus could be operated reliably up to 1.5 kbar. The radiation source in all cases was a 6 W low-pressure mercury arc lamp (254 nm) fixed at 1 cm from the sapphire window.

Arene–Ethene Systems and Analytical Methods.—The effect of pressure on the photocycloadditions of ethenes to arenes involved inter- and intra-molecular systems that we have studied extensively at 1 bar (see references in the text). The solutions were 1.0 mol dm^{-3} arene and 3.5 mol dm^{-3} ethene in acetonitrile and/or methylcyclohexene for the intermolecular systems and 1% w/v for the bichromophores. The reactions were carried out a minimum of three times at 1 bar and at the elevated pressure in the high pressure cell. The adducts were detected and identified by their chromatographic properties and their characteristic mass spectral fragmentation patterns (GC/MS). The analytical instrumentation comprised a Hewlett-Packard 5790A gas chromatograph fitted with a flame ionisation detector, and a Perkin-Elmer 8500 gas chromatograph fitted with an ion trap detector (CI mode, isobutane as reagent gas): both instruments were fitted with a 12 m × 0.35 mm i.d. BP1 (SGE OV1 equivalent) capillary column, and 2,2,4,4,6,8,8-heptamethylnonane was used as the internal GC standard.

Acknowledgements

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