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FACTORS INFLUENCING THE RELATIVE TENDENCIES FOR ortho AND meta CYCLOADDITIONS OF ETHYLENIC COMPOUNDS TO THE BENZENE RING

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Abstract In view of certain recent and seemingly incongruent reports concerning the photoaddition of ethylenic compounds to the benzene ring, the present state of knowledge about the factors influencing the addition mode, stereoselectivity, and regioselectivity of these complex processes is discussed, with particular reference to orbital symmetry and polarity considerations, the types of intermediates believed to be involved, and the effects of substituents.

The current wide-spread interest in the photocycloaddition reactions of aromatic systems with ethylenes[1-3] has its origin in the observation, reported almost three decades ago, that ultraviolet irradiation of solutions of benzonitrile and alkenes resulted in 1,2-photoadditions.[4] In 1959, Angus and Bryce-Smith reported the photoaddition of maleic anhydride to benzene via a presumed initial ortho cycloaddition,[5] and a 9,10-photoadduct of maleic anhydride and phenanthrene was described shortly afterwards.[6] Independently, Schenck[7] and Grovenstein[8] have reported similar results and several groups have since described a variety of aspects of this reaction.[1-3]

In 1966, two groups independently reported that certain alkenes also undergo meta photocycloaddition to the benzene ring.[9,10] The factors that determine whether a given combination of alkene plus aromatic compound undergoes ortho or meta cycloaddition, or both, were subsequently surveyed by an orbital symmetry analysis[11] from which it was concluded that whereas the meta cycloaddition of an S_0 alkene to S_1 benzene was allowed as a fully or partly concerted process, the corresponding ortho addition was forbidden, contrary to the Woodward-Hoffmann rules (which had been derived for aliphatic systems). The same analysis suggested that ortho cycloadditions would tend to be favoured by charge transfer either to or from the aromatic ring, or by reaction of S_0 benzene with S_1 alkene. Examples of the latter process have recently been reported[12] and moreover Houk[13] has undertaken a theoretical appraisal of ortho and meta cycloadditions which somewhat differs from the original approach.[11]

The first evidence for the involvement of polar factors in ortho cycloadditions was provided by the observation that the photoaddition of maleic anhydride to benzene involved photoexcited charge transfer between the reactants.[14] In 1974, more detailed evidence was presented that the ortho cycloadditions do indeed tend to occur most readily with ethylenes having marked donor or acceptor properties relevant to benzene,[15] and it was reported that in the cases studied up to that time, $\Phi_{ortho} > \Phi_{meta}$ when $9.6 <$ I.P. (ethylene) < 8.65 eV. Moreover, the stereoselectivities of *ortho* cycloadditions depend on the donor/acceptor properties according to this proposal.[15] Subsequent reports[2] have shown that the ionization limits in the original version of the relationship 'are too restrictive'. Although increase in ΔI.P. was shown to be validly associated with an increase in *ortho*/*meta* ratios within a series of ethylenes[2] and arenes[16] there are some exceptions concerning both the modes of cycloaddition and the stereoselectivities.[17]

What could be the reason for these exceptions of the otherwise beautifully simple ΔI.P. relationship? Ionization potentials relate to properties of the ground state of the reactants rather than of the excited state. Although different mechanisms have been proposed at least for the *meta* cycloaddition,[2] that one involving an excited state intermediate (exciplex) provides a rationalization which currently fits the experimental evidence most sufficiently (equat. 1).

$$\text{Arene} + \text{Alkene} \longrightarrow (\text{Arene} \ldots \text{Alkene})^{*} \longrightarrow \textit{meta}\ \text{Cyclisation} \longrightarrow \text{Products} \qquad (1)$$

Intermediates of this type have been proposed earlier by Morrison[18] and by Srinivasan.[19] Their existence and their role as reactive intermediates were proven later[20,21] and meanwhile numerous investigations supporting this mechanism have been reported by various groups.[2,3,13,22-26] According to Weller[27] and Mataga[28] bonding in exciplexes of acceptor (A) and donor (D) molecules is determined by the coupling between local excited states and the charge transfer state (equat. 2).

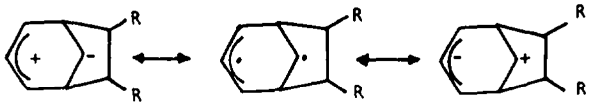
$$(A^{*}D) \longleftrightarrow (AD^{*}) \longleftrightarrow (A^{\cdot -}D^{\cdot +}) \qquad (2)$$

The energy of $(A^{\cdot -}D^{\cdot +})$ is related to the free enthalpy of electron transfer (ΔG) which can easily be calculated according to Weller.[29] Equat. 3 shows a simplified version of the so-called Weller-equation with $E^{Ox}_{1/2}$ (D)/$E^{Red}_{1/2}$(A) = redox potentials of D/A, ΔE_{excit} = excitation energy of the electronically excited species, and ΔE_{coul} = Coulomb interaction energy in a given solvent.

$$\Delta G = E^{Ox}_{1/2}\ (D) - E^{Red}_{1/2}\ (A) - \Delta E_{excit} + \Delta E_{coul} \qquad (3)$$

ΔG-values of various arene/olefin systems have been correlated with the modes of reaction and clearly show that the *meta*/*ortho* ratio increases if ΔG increases as well.[17] Moreover, this rationalisation also includes substitution reactions of arenes and olefins which are preferred in systems of exergonic electron transfer ($\Delta G < 0$)[17] and even stereochemical effects of cycloadditions appear somewhat clearer.[17,25,30] Therefore, the reason that in a given series most examples fit the ΔG correlations may be put down to the fact that here the charge transfer within excited state intermediates is considered.

In addition to primarily formed exciplexes, intermediates such as a biradical (I) have been proposed.[11] These are not necessarily electronically symmetrical, especially when strong perturbing groups are present. As previously proposed,[23,31] the intermediate species may be represented as a resonance hybrid, as follows.



(Ia) (I) (Ib)

(II)

The spin-paired canonical forms (Ia) and (Ib) might be thought more consistent with a singlet intermediate, but Reedich and Sheridan have recently generated hydrocarbon intermediates of this type from azo-precursors by direct and sensitized procedures expected to give singlet and triplet biradical species respectively, and report that they show closely similar behaviour which is virtually identical with that of the intermediates postulated to be formed directly in meta cycloadditions.[32]

The Reading group also noted that the orientation observed in the meta photoaddition of cyclopentene to toluene was consistent with an intermediate polarized as in (Ib) rather than one of prefulvene (II) type.[31]. Earlier, it had been shown that a meta cycloaddition (ethyl vinyl ether to anisole) could be susceptible to the effect of polar solvents:[33] and though this appears to be exceptional, other workers have also subsequently sought to rationalize orientation effects in additions to benzene bearing strongly perturbing substituents in terms of type (Ib) intermediates.[24-26,30] The regioselectivities of photocycloadditions of olefins to donor- and acceptor-substituted arenes are described in detail elsewhere.[34]

We now consider the mechanistic issues concerning meta cycloadditions that one of us has recently raised.[17] In order to correct any possible misunderstandings, we wish to make it clear that although the Reading group considered a mechanism via a prefulvene intermediate (II) in their original 1966 report of meta cycloaddition,[9] and have mentioned it subsequently in reviews and original papers, their further research necessitated an alternative mechanism involving direct addition of the alkene to S_1 benzene,[1-3,16,35] which was first shown in a 1969 orbital symmetry analysis[11] to be equally well allowed as a concerted process. To some extent this mechanism is similar to the 'exciplex mechanism' (see above). The Reading group noted that this could satisfactorily rationalize all the existing findings.[22]

In summary, all the mechanistic and preparative studies so far reported are consistent with the operation of mechanisms involving singlet excited state intermediates. Although some details still await clarification, orbital symmetry considerations and the degree of charge transfer between the ethylenic and aromatic addends, and within the benzene moiety of the intermediates, determine the relative tendencies for ortho and meta modes of addition, and for endo and exo stereoselectivity. Regioselectivities in the meta cycloaddition to benzenes depend on partially polarised 'biradical' intermediates of which (Ib) may represent a preferred canonical form when substituents are present that can stabilise one or both charged centres by electron delocalization.

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