Mechanism of Photochemical *meta*-Cycloaddition of Alkenes to the Benzene Ring: a Novel Type of Molecular Interaction

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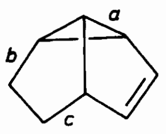
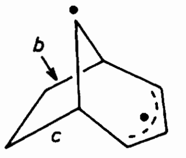
The regioselectivity of photochemical *meta*-cycloaddition of alkenes to alkylbenzenes changes progressively from 2,6- to 3,5- with increasing size of the alkyl group(s) while retaining *endo* stereospecificity: this finding implies a novel type of weak but orienting intermolecular bonding interaction (intermolecular hyperconjugation) between S_1 benzene and α-hydrogens on the alkene which can predominate over steric effects of bulky alkyl groups.

The mechanism of *meta*-photocycloaddition of alkenes to the benzene ring giving adducts of type (**1**) has been much debated since the discovery of this unusual reaction in 1966.[1] Orbital symmetry and stereospecificity considerations indicate that the process is either one in which all three new bonds *a*, *b*, and *c* are formed concertedly, or where either bond *a* alone, or *b* and *c* together, are formed initially in sequential concerted processes.[2] The mechanism currently favoured by most workers involves collapse of a benzene–alkene exciplex to form bonds *b* and *c* concertedly and a singlet diradical species (**2**).[3] Some workers write this as a zwitterion;[4,5] and singlet diradicals of this type may well be polarised to some extent (depending especially on the nature of any substituents), but be capable in principle of reacting either as zwitterions or diradicals.

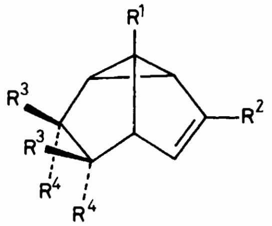
We previously reported that whereas *cis*-cyclo-octene photoadds exclusively 2,6-*endo* to toluene, it adds mainly 3,5- to t-butylbenzene.[6] We attributed this result to the steric effect of the t-butyl group on the orientation within a precursor exciplex, and pointed out that this would require the adduct to



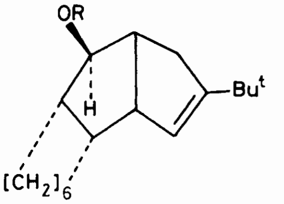
(1)



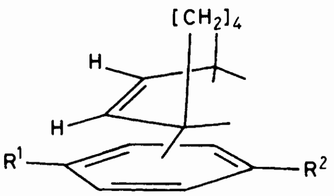
(2)



(3) $R^1 = R^4 = H$, $R^2 = Bu^t$, $R^3—R^3 = -[CH_2]_6-$
(4) $R^1 = R^3 = H$, $R^2 = Bu^t$, $R^4—R^4 = -[CH_2]_6-$
(7) $R^1 = Me$, $R^2 = Pr^i$, $R^3 = H$, $R^4—R^4 = -[CH_2]_6-$
(10) $R^1 = H$, $R^2 = R^3 = R^4 = Me$
(11) $R^1 = R^3 = R^4 = Me$, $R^2 = H$
(12) $R^1 = H$, $R^2 = Bu^t$, $R^3 = R^4 = Me$



(5) $R = -CO-NH-C_6H_4Br$-*p*
(6) R=H



(8) $R^1 = H$, $R^2 = Bu^t$
(9) $R^1 = Bu^t$, $R^2 = H$

have the *exo* structure (**3**) rather than the *endo* (**4**). However, we now unexpectedly find that the 3,5-adduct of t-butylbenzene and *cis*-cyclo-octene has structure (**4**) with the same *endo* stereochemistry as the corresponding 2,6-adduct of toluene.

This stereochemistry was unequivocally established by means of an *X*-ray crystallographic analysis of the urethane (**5**) from *p*-bromophenyl isocyanate and the acidolysis product (**6**) of the photoadduct (**4**). The crystals of (**5**) are monoclinic, space group $P2_1/a$ with cell dimensions $a = 10.114$ (8), $b = 17.200$ (8), $c = 13.165$ (11) Å, $\beta = 92.0(1)°$, $U = 2288.7$ Å^3, $D_m = 1.31(2)$, $D_c = 1.33$ g cm^{-3}, $\mu = 19.2$ cm^{-1}. 1601 Independent reflections above background were collected on a diffractometer, and the structure was determined by direct methods and refined (Br, C, O, N anisotropic, H isotropic) to *R* 0.069.† There are strong intermolecular hydrogen bonds (-NH · · · O=C) and a 30.6° twist between the phenyl ring and the N–CO$_2$ group. The *X*-ray structure of (**5**) is given in Figure 1.

Structure (**7**) was similarly established for the photoadduct of 1-methyl-4-isopropylbenzene and *cis*-cyclo-octene, corresponding to initial *endo* 2,6-addition.

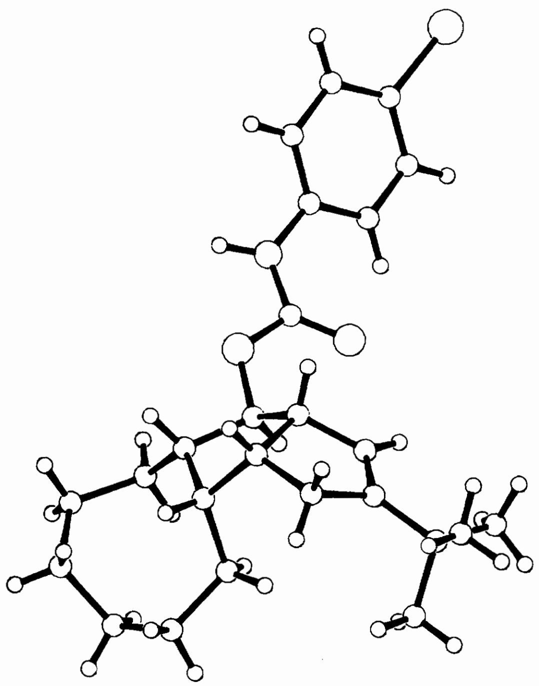


Figure 1. *X*-Ray structure of the urethane (**5**).

At first sight, the *endo* stereochemistry of the 3,5-adduct of t-butylbenzene is surprising in view of the predominantly *exo* photoaddition of 1,3-dioxoles to benzene reported by Scharf *et al.*:[3b] an *exo* photoaddition of *cis*-cyclo-octene to t-butylbenzene, giving (**3**), would avoid steric interaction with the bulky t-butyl group. The fact that the sterically less favoured *endo* addition occurs exclusively in practice requires the existence of some additional bonding interaction between the alkene and S_1 t-butylbenzene which occurs only in the *endo* orientation. This clearly cannot directly involve the C=C bond of the alkene, which interacts similarly in the *endo* and *exo* configurations, so it must involve an interaction between the α-hydrogens and the 2,6-positions of t-butylbenzene, as depicted in (**8**). Space-filling and Dreiding models confirm that this interaction should involve less repulsive interaction with the t-butyl group than in the corresponding 2,6-*endo* orientation (**9**).

To our best knowledge, this is the first evidence which clearly implies secondary bonding intermolecular interaction between a CH$_2$ group and an aromatic ring; *cf.* ref. 7 and p. 1645 in ref. 8. This interaction might be regarded as a weak type of hydrogen bonding between sp^3 and sp^2 carbon atoms, or more realistically as a form of 'intermolecular hyperconjugation' involving a minor degree of electron donation from a group orbital of p-type symmetry on CH$_2$ into the lowest partly-filled orbitals of the benzene ring. Although presumably weak it is evidently sufficiently strong to direct *meta*-cycloaddition to benzenes along the sterically less favourable *endo* pathway. Where α-hydrogen is absent, either the addition is predominantly *exo* (as with dioxoles)[3b] or fails to occur (as with di-t-butylethylenes[9]).

Photoaddition of tetramethylethylene to toluene gives the adducts (**10**) and (**11**) in a *ca.* 1 : 1 ratio *via* initial 3,5- and 2,6-addition respectively; t-butylbenzene gives only the 3,5-adduct (**12**). This departure from the exclusive 2,6-addition of *cis*-cyclo-octene to toluene probably results from the greater steric requirements for addition of tetramethylethylene (rendered even greater for the corresponding additions to t-butyl-

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

benzene), and the fact that steric repulsions in 2,6-addition would apply to the primary bonding to C=C in the alkene, but only to the secondary allylic bonding in 3,5-addition.

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