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# STERIC EFFECTS IN THE META PHOTOCYCLOADDITION OF ETHYLENES TO ALKYLBENZENES

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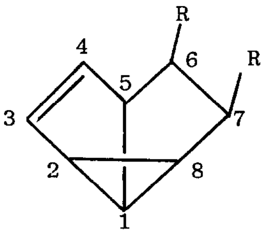
Summary: Vinyl acetate and cis cyclo-octene undergo regioselective meta photocycloaddition to alkylbenzenes: the orientation of attack suggests that adduct formation can occur by two different mechanisms.

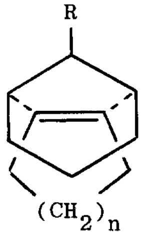
The photoaddition of cyclobutene[1] and cyclopentene[2] to toluene and the xylenes yields meta cycloadducts of type (1) which have exclusively endo stereochemistry and in which a methyl group is specifically located on the 1-position of the adduct. These results are reasonably explained by involvement of the sandwich exciplex (2) which yields (1) by 2,6-cycloaddition followed by formation of the ethenyl cyclopropane system.[2] It has been noted, however, that $S_1$ benzene should be potentially meta bonding and in principle could transform adiabatically into the ground state diradical (3) which has been termed "prefulvene".[3] Orbital symmetry correlation diagrams for the meta photocycloaddition indicate that the process is allowed both for ethylene photoaddition followed by ethenyl-cyclopane formation and for prior photoformation of prefulvene and subsequent addition of the ethylene to this diradical.[4] An indication that this latter mechanism may be operative in some systems was provided by the exclusive formation of the 5-methyl isomer of (1) from toluene and cis cyclo-octene.[5]

We have investigated the orientational selectivity of the meta photocycloaddition of toluene, isopropylbenzene, t-butylbenzene, and p-isopropyltoluene to vinyl acetate and cis cyclo-octene[6] in an attempt to establish the extent of involvement of the "sandwich exciplex" and "prefulvene" mechanisms in these processes and, more particularly, to assess if the steric bulk of the arene substituent and that of the ethylene can influence which of the two mechanisms will be preferred.

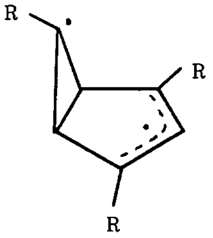
The adducts were prepared by 254 nm irradiation of equimolar mixtures of the arene and ethylene under air.[7] Adduct structures were deduced from



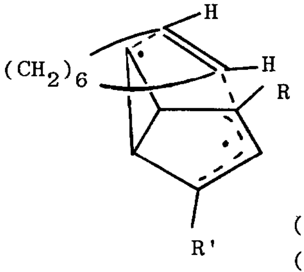
(1) R = ethylene substituent



(2) n = 0 or 1



(3)



(4) R = Me, R'=H

(5) R=H,R'=iPr or tBu

their n.m.r. spectra (CDCl$_3$ 100MHz or 220MHz[8]) and their comparison with spectra of adducts of known structure.[2,9] The results are summarised in the Table. From thermal stabilities of the adducts,[10] it is assessed that the predominant if not exclusive stereochemistry of cycloaddition of cis cyclo-octene to the arenes is endo and that > 80% of the vinyl acetate-arene meta adduct mixture has the acetate group endo at C-7.

TABLE

meta-Cycloaddition of Vinyl Acetate and cis-Cyclo-octene to Alkylbenzenes

| | Substitution position on meta cyclo-adduct (1) | |
|---|---|---|
| Arene | Vinyl acetate† | cis Cyclo-octene |
| | (approximate respective ratios) | |
| Toluene | 1-methyl | 5-methyl[6] |
| iso Propylbenzene | 1-isopropyl, 3-isopropyl,<br>(4:1) | 1-isopropyl,3-isopropyl<br>(2:1) |
| t-Butylbenzene | 1-t-butyl,3-t-butyl,<br>(3:1) | 1-t-butyl, 3-t-butyl<br>(1:1.5) |
| p-isoPropyltoluene | 1-methyl-3-isopropyl,<br>1-isopropyl-3-methyl,<br>(2:1) | 1-methyl-3-isopropyl,<br>1-isopropyl-3-methyl,<br>(5:1) |

† Polymer formation increased with increase in size of arene substituent.

With the exception of toluene and *cis*-cyclo-octene, the *meta* cycloadditions are remarkably selective yielding only the 1- and 3-substituted isomers of (1) which reflect 2,6- and 3,5- attack of the ethylenes respectively.[11] Formation of the 1-isomers is consistent with the proposal[2] of an intermediate 2,6-oriented *endo* sandwich exciplex preceeding the addition step but it is most unlikely from steric considerations that an analogous *endo* species would be involved in the 3,5-attack, particularly in the case of *cis* cyclo-octene, and yet *endo* stereomers are preferred and this mode of reaction becomes relatively more favoured as the steric effects increase. Further, it is significant that with *p*-isopropyltoluene, the isomer of (1) which predominates is that with the isopropyl group in the 3- rather than the 1- position and that this effect is more pronounced with *cis*-cyclo-octene than with vinyl acetate. Quantum yields for *meta* cycloadduct formation for both ethylenes do decrease with increase in size of the arene substituent. However, although $\Phi_{total}$ for *cis*-cyclo-octene and *t*-butylbenzene is half of that for this ethylene and benzene,[12] $\Phi_{total}$ for the corresponding addition to *p*-isopropyltoluene is actually 20% greater than for the unsubstituted arene. The above data suggest the variable involvement in *meta* cycloadditions of a primary intermediate such as the prefulvene diradical (3), the formation of which, unlike the sandwich exciplex, is not greatly affected by steric factors but indeed which becomes relatively more favoured over the latter species with increase in size of the arene and/or ethylene substituent(s). Such a species as (3) would be stabilised by substitution at the indicated positions and it is significant that the 3,5,8-trimethyl isomer of (1) comprises a third of the *meta*cycloadduct mixture from mesitylene and cyclopentene.[2] For mono substituted benzenes formation of (3) with the substituent in the 5-membered ring seems to be favoured since no 8-monosubstituted isomer of (1) has been detected from ethylenes and alkylbenzenes. Formation of the 5-methyl isomer of (1) from toluene and *cis* cyclo-octene may be accounted for by the prefulvene intermedicate as shown in (4) but it appears that for bulkier substituents than methyl, the approach of the ethylene is changed to that in (5) which results in the formation of the 3-isomer of (1).

To summarise, our results show that *meta* cycloaddition of ethylenes to substituted benzenes is a regioselective rather than regiospecific process. In order to account for the positional isomers of (1) which are formed, it is necessary to consider two basic mechanisms, one which involves prior orientation of the addends possibly in an exciplex and this leads to the 1-substituted isomer of (1) and the other in which the ethylene adds to a photoproduced bicyclo [3.1.0]hexenyl diradical which yields the 3- and 5-isomers of (1). The mechanistic pathway followed, can, seemingly, be influenced by steric considerations of the arene and/or ethylene.

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6. The 254 nm irradiation of cyclopentene with isopropylbenzene *t*-butylbenzene or *p*-isopropyltoluene gave relatively low yields of multicomponent mixtures of which 1:1 adducts constituted $\not<$ 50%.

7. Minor amounts of photoproducts other than *meta* cycloadducts were also formed but their concentrations were sufficiently low not to interfere seriously with spectral interpretations.

8. P.C.M.U. Harwell are thanked for the 220 MHz n.m.r. spectra.

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