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# meta-PHOTOCYCLOADDITION OF ETHYLENES TO SUBSTITUTED BENZENES

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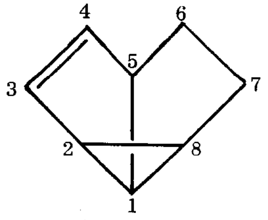
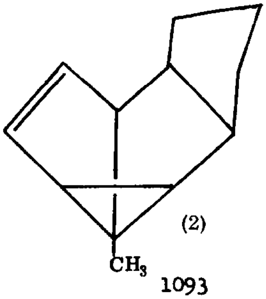
Although the photochemical meta-cycloaddition of ethylenes to the benzene ring, giving adducts of type (1), was first reported over ten years ago,[1] many features of this intriguing process remain to be clarified.[2] It does however appear to require (a) $S_0 \rightarrow S_1$ excitation of the arene rather than the ethylene, and (b) closely similar ionisation potentials for the arene and a mono-ethylenic addend: otherwise ortho and para additions become important, and may even constitute the exclusive reaction mode(s).[3]

The process appears to be generally stereospecific with respect to the ethylene, but Srinivasan and co-workers have also reported meta-cycloadditions of cyclobutene[4] and cyclopentene[5] to methylbenzenes, and cis-but-2-ene and various cycloalkenes to anisole,[6] in orientations which are remarkably specific with respect to the position of the substituent in the benzene ring; and endo isomers were reported to be formed exclusively from methylbenzenes and, possibly so, from anisole. Our own findings, now reported, show that the meta- cycloaddition reaction can exhibit features which differ markedly from those indicated by the work of Srinivasan et al.[4,5,6]

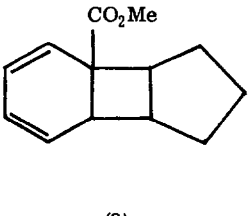
In particular, we find that the orientation in meta-cycloaddition to toluene and m-xylene can depend greatly on the nature of the ethylene. For example, whereas we confirm the previous report that cyclopentene photoadds 2, 6- to toluene to give the endo adduct (2),[5] we have observed that cis-cyclo-octene adds virtually exclusively 1, 3- to give a 7:1 mixture of endo and exo adduct respectively. A similar 7:1 mixture is produced by the 2, 6-photoaddition of cis-cyclo-octene to p-xylene. (The endo and exo adducts are readily distinguished by their different thermal labilities.[7]) In meta-photoadditions of cyclopentene and cis-cyclo-octene to o- and p-xylenes, the orientations are



(1)



(2)



(3)

the same with respect to the methyl groups, but in the case of *m*-xylene they are totally different. These results are summarised in the Table.

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Table: *meta*-Cycloaddition of Cyclopentene and *cis*-Cyclo-octene to Methylbenzenes

| Arene | ΔI. P. (eV)[a] | | *meta*-Adducts of type (1) | |
|---|---|---|---|---|
| | $C_5H_8$ - arene | $C_8H_{14}$ - arene | From $C_5H_8$(addition mode)[5] | From *cis*-$C_8H_{14}$ (addition mode) [b, c] |
| Toluene | 0.2 | 0.07 | 1-methyl (2, 6-) | 5-methyl (1, 3-) |
| *o*-Xylene | 0.46 | 0.21 | 1, 5-dimethyl (1, 3-)<br>1, 8-dimethyl (1, 3-)<br>(3:1)[d] | 1, 5-dimethyl (1, 3-)<br>1, 8-dimethyl (1, 3-)<br>(3:2)[e] |
| *m*-Xylene | 0.44 | 0.19 | 1, 4-dimethyl (2, 4-)<br>1, 2-dimethyl (2, 4-)<br>(4:3)[d] | 2, 4-dimethyl (4, 6-)<br>3, 8-dimethyl (1, 5-)<br>(6:7) [e, f] |
| *p*-Xylene | 0.58 | 0.31 | 1, 3-dimethyl (2, 6-) | 1, 3-dimethyl (2, 6-) |

[a] All the ionisation potential differences are low and in the range where *meta*-cycloaddition would be predicted to predominate according to the mechanistic proposals in ref. 3 . In fact, no adducts other than those of *meta* type were detected; but see *f*.

[b] The numbering for the addition mode refers to the *meta* positions in the aromatic ring to which the ethylene becomes attached: the numbering for the adducts refers to structure (1). Note that some nominal *meta*-additions of a symmetrical ethylene could in principle lead to two isomeric adducts of type (1) : *e.g.* 1, 3-addition to toluene could in principle give adducts having the methyl group at either $C_5$ or $C_8$ in (1) ; but 2, 6-addition could give only one adduct having methyl at $C_1$ .

[c] Arene-cyclo-octene solutions 1:3 by volume, low pressure Hg arc lamp, structures deduced from spectroscopic properties, in particular the n. m. r. spectra .

[d] Ratios of upper to lower isomers isolated .

[e] Ratios of upper to lower isomers detected (analytical g. l. c. ) ; isolation by preparative g. l. c.

[f] These adducts comprised approximately 65% of the reaction mixture. The remaining 35% comprised five other 1:1 adducts in minor amounts. This mixture of minor adducts was unaffected by treatment with N-phenylmaleimide, so probably did not contain *ortho* cycloadducts.

The total quantum yields for the meta- cycloadditions of cis-cyclo-octene to toluene and o- and p-xylenes are ca. 0.3 - 0.32, and compare well with the figure of 0.37 reported for the addition to benzene under similar experimental conditions,[3] but the addition to m-xylene is less efficient ( $\Phi = 0.2$).

Additions of Cyclopentene to Other Arenes. We have also studied the 254-nm irradiation of mixtures of cyclopentene with fluorobenzene, benzotrifluoride, chlorobenzene, bromobenzene, iodobenzene, methyl benzoate, aniline, N-methyl- and NN-dimethylaniline, trimethylanilinium iodide, phenyl acetate, nitrosobenzene, and biphenyl (with and without cyclohexane, methanol, acetonitrile and diethyl ether as diluents). Only with the first two of these arenes were meta-cycloadducts observed among the products, and their formation was largely independent of the presence, absence, or type of solvent. The meta-additions to these two arenes were rather unselective ; thus fluorobenzene for example gave two positional isomers of the basic structure (1), the thermal instability of which has so far prevented unambiguous location of the fluorine substituent.[8] All the halobenzenes gave mixtures of products formed by C-Hal addition: these will be described elsewhere. Benzotrifluoride gave six meta-adducts. At least one of these has a vinylic $CF_3$ group and therefore results from a mode of meta addition not previously reported for a monosubstituted benzene (contrast ref. 5). Methyl benzoate gave the ortho cycloadduct (3) as the main product together with two minor as yet unidentified 1:1 adducts. The other arenes gave no detectable amounts of products apparently derived from reactions with cyclopentene.

The following conclusions may be drawn from this work.

1. In photoreactions of toluene and the xylenes with cyclopentene and cis- cyclo-octene, meta- cycloadditions occur virtually exclusively. This finding is consistent with the previous prediction of predominant meta-cycloaddition in systems where $\Delta$ I. P. is small (< ca. 1 eV).[3]

2. Ionisation potentials are less helpful in predicting the tendency for meta-cycloaddition when the arene bears chlorine, bromine, or iodine substituents, or substituents containing N and O heteroatoms. The reasons for this will be discussed in the full paper.

3. The orientation of meta- cycloaddition can depend critically on the nature of the ethylene. The 1-position in the meta- adducts (1) from methylbenzenes does not invariably bear a methyl group, and the deactivation of positions meta to the methyl group in toluene reported in ref. 5 does not apply with cis- cyclo-octene as addend.

4. In the meta- cycloadditions, there is a preference for endo stereochemistry, but in contrast with the reports in refs. 4 and 5 this is not always exclusive with toluene and the xylenes.

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8. In contrast, the adducts from meta-photoaddition of vinyl acetate to fluorobenzene are more thermally stable, and can readily be distilled. (A. Gilbert, M. W. bin Samsudin Angew. Chem. Internat. Edn., 1975, 552).