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MECHANISM OF THE PHOTOCHEMICAL META-CYCLOADDITION OF ALKENES TO THE BENZENE RING

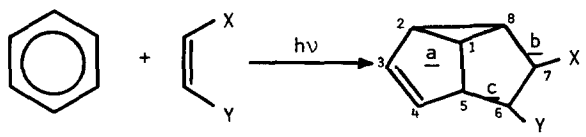
D.Bryce-Smith, G.A.Fenton, and A.Gilbert

Chemistry Department, University of Reading, Whiteknights, Reading, Berkshire,RG6 2AD.

Summary: The mechanism of photochemical meta-cycloaddition of alkenes to arenes is considered in the light of new observations concerning the effects of bulky substituents.

The surprisingly efficient meta-photocycloaddition of alkenes to arenes, discovered by two independent groups in 1966,[1,2] still presents mechanistic problems. The main uncertainties concern (i) the possible intermediacy of exciplexes, and (ii) the relative timing of the three bond-making steps. We report herein evidence mainly concerning (ii).

The process can in general be represented as follows:



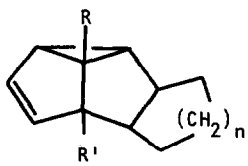
(1)*

From an orbital symmetry viewpoint, it has been shown that the following three alternatives are symmetry-allowed from S_1 benzene + S_0 alkene: (A) bond a formed prior to b and c; (B) bonds b and c formed concertedly, but prior to a; and (C) bonds a, b and c formed in a fully concerted manner.[3] Alternative mechanisms involving triplet species, alkene excitation, or photochemical charge-transfer excitation have been ruled out.[4] Moreover, the high stereospecificity of the addition with respect to the alkene requires that bonds b and c at least are formed in a concerted manner.[4]

We previously reported that cyclopentene and cis-cyclo-octene differ in the orientations of their meta-cycloadditions to toluene and anisole,[5] and suggested that this difference could be explained by the operation of mechanism (B) with cyclopentene, and (A) with cis-cyclo-octene. Thus cyclopentene added 2,6- to toluene giving (2) whereas cis-cyclo-octene appeared to add 1,3-, giving (3).

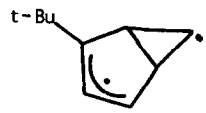
However since structure (4) has recently been assigned to the toluene-cyclo-octene adduct by Sheridan, largely on the basis of 270-MHz n.m.r. spectra,[6] we have re-examined our previous structural evidence which had been based on 100-MHz n.m.r. spectra and comparison of chemical shifts with those reported for related structures.[7] The critically important coupling between protons on C(4) and C(5), which we have confirmed to be not perceptible in a 100-MHz spectrum, does indeed appear at 220 MHz, as at 270 Hz. Structure (3) must accordingly be withdrawn in favour of (4). For similar reasons, the adduct from anisole and cis-cyclo-octene must now be assigned structure (5), in agreement with Sheridan.[6]

* Footnote: This numbering differs from that of some other workers who in cases where X-Y = $-(CH_2)_n-$ have included the methylene chain in the numbering system. The present system is more suitable for general use.



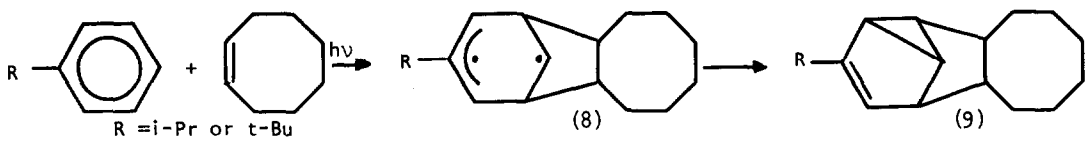
(2) R=Me, R'=H, n=1
(3) R=H, R'=Me, n=4
(4) R=Me, R'=H, n=4
(5) R=OMe, R'=H, n=4

(6)



(7)

At first sight, these observations appear to rule out the operation of mechanism (A), leaving only (B) or perhaps (C): the reasoning is described in refs. 5 and 8. We have however observed an unexpected effect of increasing the bulk of the alkyl group which is not clearly explicable on the basis of this reasoning. Any initial 2,6- interaction with the alkene (or an exciplex) would presumably have to be represented as e.g. (6), following Srinivasan,[7] because the addition has endo stereospecificity. But since any other mode of endo-meta interaction than that depicted in (6), viz. 1,3-, 2,4-, or 3,5-, would involve a greater degree of steric interaction with the substituent R, increasing the size of R from methyl through isopropyl to t-butyl would not be expected to change any endo orientation, viz. that corresponding to an initial 2,6-interaction, though it might perhaps be expected to reduce the quantum yield for an endo addition. In practice, we find that the orientation does change to produce increasing proportions of the 3-substituted isomer that would result from initial 3,5-addition according to mechanism (B), as follows, or addition to (7) via mechanism (A). With R = methyl, isopropyl, and t-butyl, the ratios of the 1- and 3-



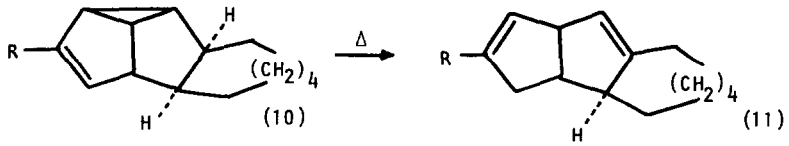
substituted adducts with cis-cyclo-octene are 1:(0), 2:1, and 1:1.5 respectively, and the corresponding relative quantum yields for total meta adducts are (1), 0.45, and 0.33: the corresponding figure for benzene is 0.75 (Ψ = 0.38).

These are in fact the first examples of the production of 3-monosubstituted derivatives of (1). The orientation would be consistent with mechanism (A) but is less in accord with (B) since the group R in (8) is not in a position where it would tend to stabilise the allylic radical (or carbocation in a corresponding zwitter-ion).

In order to ascertain whether the 1- and 3-isomers are being formed by different mechanisms [e.g. by mechanisms (B) and (A) respectively], we examined the effects of temperature and solvent polarity on the isomer ratios for the meta adducts from isopropylbenzene and t-butylbenzene with cis-cyclo-octene. An increase in reaction temperature over the range 10-120° caused a progressive reduction in the quantum yields, the factor being 10 at 120°, but the relative quantum yields for the 1- and 3-isomers remained unchanged within experimental error ($\pm$ 5%). A change in solvent from cyclohexane to acetonitrile had no discernible effect on quantum yields. We conclude therefore that the 1- and 3-isomers are derived from the same intermediate or from closely similar intermediates, and that such intermediates are essentially non-polar.

The most economical explanation for the formation of 3-isomers (9) is that the ethylenic bond in an exciplex (6) becomes displaced towards the 3,5-positions of the

benzene ring when R is a bulky group. This explanation however requires that the resulting adduct should have the exo structure (10), whereas benzene and toluene largely give endo-adducts:[4,8] with benzene and cis-cyclo-octene for example, the exo/endo ratio is ca. 0.18.



Hitherto, it has proved simple to distinguish between endo and exo isomers of this type because only the latter can undergo an allowed 1,5-suprafacial hydrogen shift at 250-300°, e.g. (10)→(11), whereas the former are stable under these conditions.[9] Application of this test to the mixture of 1- and 3-derivatives of (1) formed from t-butylbenzene and cis-cyclo-octene confirmed that the 1-isomer had endo stereochemistry, as expected. The 3-isomer was thermally less stable than the 1-isomer, in agreement with the exo stereochemistry derived from the foregoing mechanistic model. However, rearrangement of the 3-isomer required a temperature of 330°, which is higher than that normally needed for an exo adduct, and gave moreover a mixture of at least three isomeric products, as yet unidentified, whereas the thermal sigmatropic rearrangement of analogous exo isomers normally gives a single product of type (11). Inspection of models does however suggest that the bulky t-butyl group might significantly hinder the suprafacial passage of hydrogen during a 1,5-sigmatropic rearrangement, thereby conferring greater thermal stability and conceivably diverting the reaction pathway.

Unfortunately, the analysis of ^{1}H n.m.r. spectra has not yet permitted an unambiguous distinction to be drawn between endo and exo adducts of this type, so assignment of the expected exo stereochemistry to the 3-isomers must remain probable but tentative. It should be noted that the 3,5-mode of exo meta addition is less subject to the steric influence of the t-butyl group than any other mode of exo addition. Thus although 2,4-exo addition could give an energetically favoured tertiary radical centre in a mechanism (B) intermediate, it appears in this case that the steric factor is dominant; but radical stabilisation appears largely to determine the orientation of meta addition in the absence of a bulky group.[7]

Thus far, the findings can be satisfactorily rationalised in terms of a type (B) mechanism involving an initial interaction between S_1 benzene and S_0 alkene. But a serious difficulty in the acceptance of this has been previously noted,[4] but never satisfactorily explained, viz. the virtual failure of simple alkenes to quench benzene fluorescence.[10] It is clear that the excited states involved in fluorescence and meta-cycloaddition are not identical, and since fluorescence proceeds from the lowest vibrational level of the S_1 arene, one might conclude that meta-cycloaddition involves upper vibrational levels of the S_1 arene, as does the formation of benzvalene and fulvene via 1,3-bonding.[11] But the species which undergoes meta cycloaddition evidently differs from that which undergoes intramolecular 1,3-bonding since the former process is favoured at longer, and the latter by shorter, wavelengths within the $S_0 \rightarrow S_1$ band.[11] We suggest that these apparent contradictions can be reconciled if meta cycloaddition is favoured by low vibrational levels of the S_1 arene: at higher levels, the system S_1 arene + S_0 alkene could well possess energy in excess of

the dissociation energy of the intermediate exciplex which is the favoured precursor of a meta adduct; but this restriction does not apply to intramolecular 1,3-bonding in the arene. The observation that arene fluorescence is quenched when the alkene moiety is linked to the arene by a $-(CH_2)_3-$ chain does however suggest that the vibrational ground state of the S_1 arene is not wholly unreactive.[12]

The fully concerted mechanism (C) remains to be considered. We do not exclude this, but consider it unlikely in view of the large steric requirements of the transition state, coupled with the ring strain in formation of the three new bonds, and the ability of the partly concerted mechanism (B) to account for the orienting effects of most substituents.

References

1. K.E.Wilzbach and L.Kaplan, J.Amer.Chem.Soc., 1966, 88, 2066.
2. D.Bryce-Smith, A.Gilbert, and B.H.Orger, Chem.Comm., 1966, 512.
3. D.Bryce-Smith, Chem.Comm., 1969, 806.
4. See references in D.Bryce-Smith and A.Gilbert, Tetrahedron, 1977, 33, 2459, and A.Gilbert, Pure Appl.Chem., 1980, 52, 2669.
5. D.Bryce-Smith, W.M.Dadson, A.Gilbert, B.H.Orger, and H.M.Tyrrell, Tetrahedron Letters, 1978, 1093; W.M.Dadson, A.Gilbert, and P.Heath, J.Chem.Soc.Perkin I, 1980, 1314.
6. R.S.Sheridan, Tetrahedron Letters, 1982, 267.
7. J.A.Ors and R.Srinivasan, J.Org.Chem., 1977, 42, 1321 and references therein.
8. D.Bryce-Smith, B.E.Foulger, J.Forrester, A.Gilbert, B.H.Orger, and H.M.Tyrrell, J.Chem.Soc., 1980, 55.
9. R.Srinivasan, Tetrahedron Letters, 1971, 4551.
10. A.Morikawa and R.J.Cvetanovic, J.Phys.Chem., 1968, 49, 1214.
11. L.Kaplan and K.E.Wilzbach, J.Amer.Chem.Soc., 1968, 90, 3291.
12. W.I.Ferree, J.B.Grutzner, and H.Morrison, J.Amer.Chem.Soc., 1971, 93, 5502; A.Gilbert and G.N.Taylor, J.Chem.Soc., Perkin I, 1980, 1761.

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