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A REINVESTIGATION OF THE META—PHOTOADDITIONS OF CYCLOOCTENE TO ANISOLE AND TOLUENE

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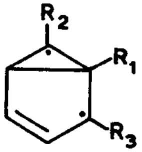
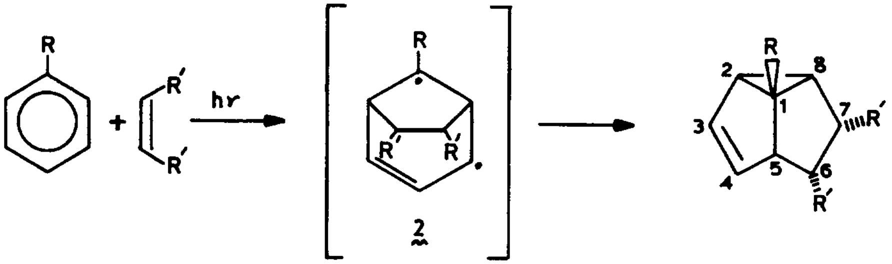
Summary The meta-photoadditions of cis-cyclooctene to anisole and toluene are shown to proceed via 2,6-bonding to the aromatic rings, in contrast to previous reports.

The 1,3- or meta-addition of olefins to singlet excited benzene derivatives has generated much interest,[1] both from a purely mechanistic standpoint and as a synthetic route to natural products [2,3] Despite extensive investigations, the mechanism of these reactions is unclear.[1] A major point of controversy centers on the timing of addition. Bryce-Smith and Longuet-Higgens made the early suggestion that the reaction began with 1,3-closure of excited singlet benzene to give biradical 1 [4] Addition of olefin across the radical centers would give the observed products. Srinivasan and coworkers showed, however, that photoadditions of a number of olefins to toluene[5] and to anisole[6] give products with the aryl substituent appearing solely at the 1-position. This regioselectivity suggested initial interaction between the olefin and the 2,6-positions of the aromatic ring, either through direct bonding to give a biradical such as 2 or via prior exciplex formation with this geometrical arrangement. In particular, the absence of corresponding 2-substituted products appeared to exclude the intermediacy of biradical 3.



1 $R_1=R_2=R_3=H$
3 $R_1=Me,R_2=R_3=H$
4 $R_3=Me,R_1=R_2=H$
5 $R_2=OMe;R_1=R_3=H$



It has recently been reported that the regiochemistry of cyclooctene photoaddition to substituted aromatic compounds is anomalous Cis-cyclooctene was suggested to add to toluene to give the 5-isomer[7], and to anisole to give 8-isomer[8]. These results have been cited as strong evidence for the intermediacy of the biradicals 4 and 5.

We now wish to report a reinvestigation of the cyclooctene photoadditions. Higher field NMR data, deuterium labelling, and chemical transformations reveal that cyclooctene adds to both toluene and anisole to give the same regiochemistry as observed for other olefins

A mixture of anisole and cis-cyclooctene (1 3 by volume) was irradiated at 254 nm for 12 h. NMR (^{1}H, 270 MHz) of the crude product mixture, after removal of starting materials in vacuo and distillation (80°C, 0.1 Torr), showed the presence of primarily two components in the ratio of ca. 7 1 (30% estimated yield of major compound). The main component, isolated by GLC (Carbowax, 185°C), exhibits an ^{1}H-NMR spectrum (Figure 1) which is quite similar to those reported by Ors and Srinivasan[6] for other cycloalkene-anisole endo-adducts, and supports the 1-isomer, 6,[9,10] NMR (270 MHz, CDCl$_3$) δ 5.71 (d of d, H-13), 5.64 (d of d of d, H-12), 3.37 (s, OMe), 3 08 (m, H-11), 2.63 (m, H-10), 2 52 (m, H-3), 2.33 (d of d, H-2), 1.98 (d of d of d, H-14), 1.75-1.00 (complex, H's at 4-9). The proton assignments were confirmed by double irradiation experiments, and by the NMR spectra (^{1}H and ^{2}D) of the analogous d$_5$-adduct from d$_5$-anisole. Several decoupling results are shown in Figure 1. The key points in locating the methoxy-substituent are. (1) Three aliphatic protons (H-2,H-11,H-14) derive from anisole; (2) Two of these protons (H-2 and H-14) are coupled to each other ($\nu_{2,14}$=8.5 Hz) and neither is coupled to the third proton (H-11), (3) H-14 is coupled to the down-field vinyl H-13 ($\nu_{13,14}$=2.3 Hz) and not to the cyclooctyl derived protons H-3 and H-10, (4) H-2 is coupled to the cyclooctane proton H-3 ($\nu_{2,3}$=6.8 Hz), and not coupled to either olefinic proton, (5) H-11 is coupled to the upfield olefinic proton, H-12, and to both H-3 and H-10 (models indicate a reasonable W-relationship between H-3 and H-11).

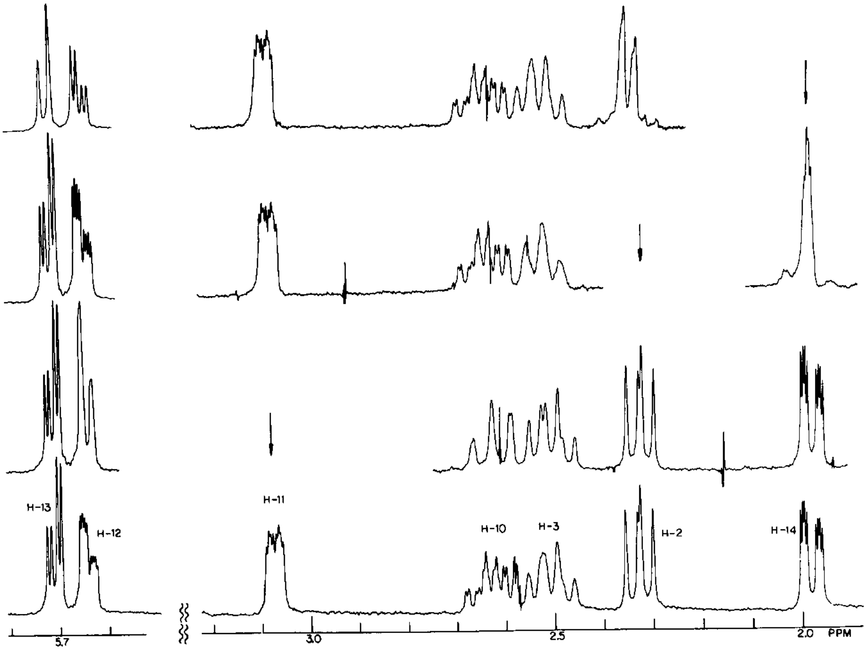
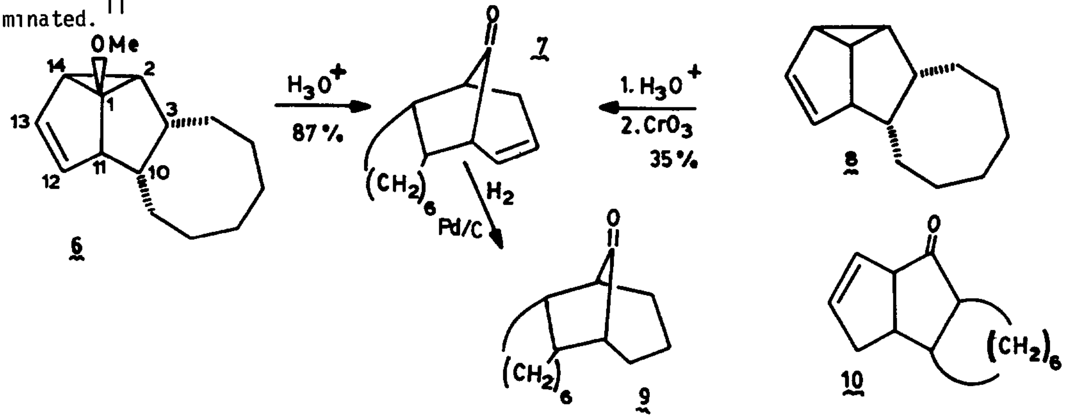


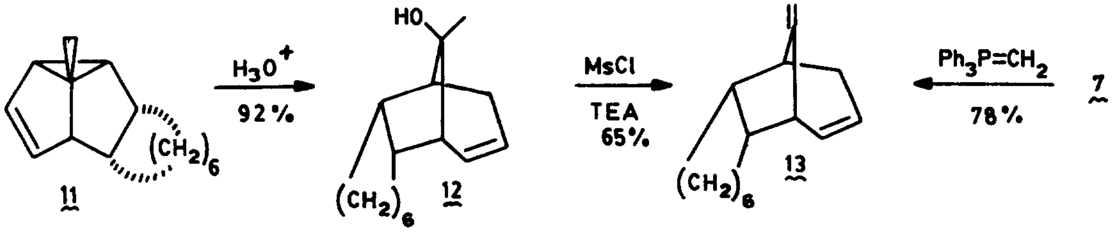
Figure 1. Bottom shows two portions of ^{1}H-NMR spectrum (270 MHz) of anisole adduct 6. Upper plots show effects of decoupling at positions shown by arrows

The position of methoxy substitution was confirmed by the chemistry of 6 Srinivasan and coworkers have shown that acid catalyzed hydrolysis of meta-photoadducts specifically effects cyclopropane cleavage to give bicyclo[3.2 1]octene derivatives.[5,6] Treatment of 6 with dilute aqueous acid in refluxing acetone cleanly gives the expected ketone 7.[11] The same ketone was generated from the endo-cyclooctene-benzene photoadduct 8, by the sequence shown. The simplification of the ^{13}C-NMR spectrum of 7 (14 lines) on hydrogenation to 9 (8 lines) lends support to the structure assignment. In particular, other possible structures such as 10 can be eliminated.[11]



Toluene and cis-cyclooctene (1:3) were irradiated and the volatile products isolated in an identical fashion as above. ^{1}H-NMR of crude distilled (68°C, 0.25 Torr) material showed mainly the presence of two isomers in a ratio of ca. 6:1 (10% estimated yield of main component).[10] The ^{1}H-NMR of the main product, isolated by GLC (carbowax, 140°C), is most consistent with the 1-isomer, 11; NMR (270 MHz, CDCl$_3$) δ 5.69 (d of d, H-13), 5.52 (d of d, H-12), 2.61 (m, H-11), 2.47 (m, H-10 and H-3), 1.67 (H-2, partially obscured by cyclooctane protons), 1.40 (H-14, partially obscured), 1.36 (s, -CH$_3$), 1.85-1.06 (complex, H's at 4-9). Although in this case the cyclopropyl protons are partially obscured by the cyclooctane ring protons, the effects of double irradiation were easily discernible. The arguments pointing to structure 11, based on ^{1}H-decoupling and ^{1}H- and ^{2}D-NMR spectra of the adduct formed from d$_8$-toluene, are exactly analogous to those listed above for 6. In particular, the H-11 proton was readily characterized by its coupling to the olefinic proton H-12 and to the cyclooctyl derived protons (H-3 and H-10), and by the lack of coupling to the cyclopropyl protons (H-2 and H-14).

The chemistry of 11 confirms the assigned structure. Hydrolysis of 11, as above, gives an alcohol whose spectra support structure 12. Formation of the mesylate and elimination in situ with triethylamine cleanly gives the diene, 13. The same diene is generated on reaction of ketone 7 with methylenetriphenylphosphorane.[11]



The above results indicate that, contrary to previous claims, *cis*-cyclooctene acts normally in photoadditions to anisole and toluene. These results thus weaken the possibility of the involvement of biradicals such as **1** in the *meta*-photoadditions in general[12,13]

References and Notes

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9. All compounds described gave satisfactory molecular formulae by high resolution mass spectrometry. NMR spectra were obtained on a Bruker WP-270 (270 MHz-^{1}H), JEOL FX-200 (31 MHz, ^{2}D), or JEOL FX-60 (15 MHz, ^{13}C). All spectra are in CDCl$_3$ (or CHCl$_3$ for ^{2}D) and are given in ppm relative to TMS.
10. The minor components were not isolated. The NMR spectra and thermal lability (ref. 1 and 5) suggest that these correspond to the *exo*-adducts.
11. **7**· ^{1}H NMR δ 5.69 (m, H-11), 5.56 (m, H-12), 2.74 (m dominated by AB, H-13α,β, ν = 17.6 Hz), 2.42 (m, H-1), 2.28 (m, H-2, H-9, H-10), 1.92-1.15 (complex, H-3 through H-8), ^{13}C δ 216.4, 130.1, 126.6, 52.1, 50.6, 43.3, 39.1, 35.2, 21.4, 30.4, 26.2, 25.9, 24.9, 24.2; mp 39-40°C; IR (CHCl$_3$) ν 1750 cm^{-1}.
    - **9** ^{13}C-NMR δ 221.5, 52.1, 37.9, 32.3, 31.2, 26.2, 22.6, 19.8.
    - **12**. ^{1}H-NMR δ 5.66 (m, H-11), 5.37 (m, H-12), 2.44 (m, H-2, H-9), 2.23 (m, dominated by AB, ν_{AB} = 18.4, H-13$_{\alpha,\beta}$), 2.00 (m, H-10), 1.82 (m, H-1), 1.41 (s, Me), 1.74-1.12 (complex, cyclooc. and OH), mp 91-93°C.
    - **13** ^{1}H-NMR δ 5.74 (m, H-11), 5.42 (m, H-12), 4.62 (br s, =CH$_2$), 2.56 (m, H-1, H-10), 2.36 (m dominated by AB, ν_{AB} = 18.1 Hz, H-13$_{\alpha,\beta}$), 2.08 (m, H-2, H-9), 1.75-1.11 (complex cyclooctyl).
12. The overall features of our ^{1}H-NMR spectrum of **6** are congruent to the values reported by Dadson, *et al* (ref. 8), save for a systematic 0.1 ppm shift upfield in our spectra. No spectra for the toluene-cyclooctene adduct (ref 7) have been reported.
13. We are grateful to the University of Wisconsin Alumini Research Foundation for support of this work.

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