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REACTIONS OF CYCLO-OCTATETRAENE AND ITS DERIVATIVES, Part VI.[1]
STEREOCHEMISTRY OF THE BENZENE-ACRYLONITRILE [2+2] PHOTO-ADDUCT.

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Light-induced 1,2-cycloaddition of olefins to benzene is an efficient process only when the olefin has marked donor or acceptor properties.[2] In contrast with 1,3-cycloaddition, only one stereoisomer of the 1,2-cycloadduct has been observed in each olefin-benzene reaction, and it appears that acceptor olefins yield exo 1,2-adducts while those with donor characteristics give endo products.[2] However, the two 1,2-cycloadducts of acrylonitrile and naphthalene have recently been assigned[3] endo stereochemistry, which is contrary to that which would be predicted by analogy with benzene-olefin systems.

In view of these results we have investigated the stereochemistry of the known 1,2-cycloadduct (I) of acrylonitrile and benzene,[4] and this has now been established as follows.

The cyclo-octatetraene-maleic anhydride adduct (II) reacts with carbon tetrachloride in the presence of benzoyl peroxide to afford the product (III), the stereochemistry of which has been determined.[1] Reaction of the trichloromethyl-anhydride (III) with concentrated sulphuric acid, followed by treatment with water, leads to the tricarboxylic acid (IV; R=H).[1] No change of stereochemistry would be expected in this conversion, and supporting evidence is provided by comparison of the n.m.r. spectra of the derived esters (IV; R=Me) and (V).

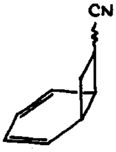
(IV; R=Me); τ 3.3 - 3.7(2H), 5.15 - 5.4(1H), 6.30(3H, s), 6.37(6H, s), 6.75 - 7.45(7H).

(V)[1]; τ 3.3 - 3.7(2H), 5.25 - 5.55(1H), 6.39(6H, s), 6.5 - 7.4(7H).

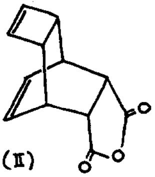
Dechlorination of the trimethyl ester (IV; R=Me) m.p. 104-106°, with tributyltin hydride[5] (in refluxing toluene, catalysed by azobisisobutyronitrile) gave a product (VI; R=Me); m.p.

86-87°, τ 3.4 - 3.6(2H), 6.34(3H, s), 6.40(6H, s), 6.85 - 7.95 (8H), 8.15 - 8.45(1H). This dechlorinated trimethyl ester was identical (mixed m.p. and comparison of n.m.r. spectra) with a sample produced by esterification of the tricarboxylic acid (VI; R=H), obtained from the photo-adduct (I) by reaction with maleic anhydride and subsequent hydrolysis of the nitrile-anhydride (VII).[4]

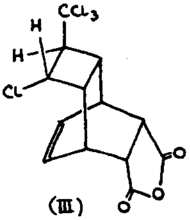
Thus the 1,2-cycloadduct of acrylonitrile and benzene has the exo configuration, in agreement with the suggested exo stereospecificity of such photo-additions of acceptor olefins to benzene.



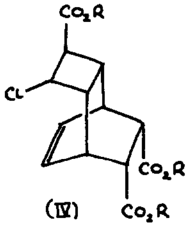
(I)



(II)



(III)



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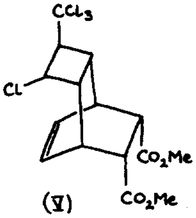
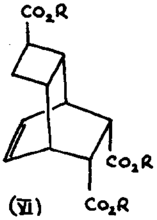
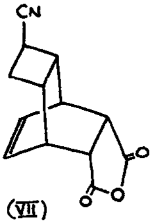


(V)



(VI)



(VII)

The two new compounds (IV; R=Me) and (VI; R=Me) gave correct analytical figures. N.m.r. spectral data refer to 100 MHz spectra and $CDCl_3$ solutions.

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