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STEREOCHEMISTRY OF THE 1,2-PHOTOCYCLOADDUCTS OF VINYL ETHERS AND BENZENE

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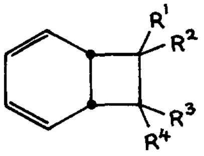
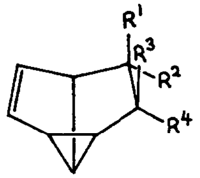
Irradiation of benzene at 254 nm. in the presence of electron-deficient ethylenes leads exclusively to 1,2-cycloadducts of structure (1).[1] The products from acrylonitrile,[2] methyl vinyl ketone,[3] maleic anhydride,[4] and maleimide[5] are formed with exo stereospecificity, while mixtures of both the possible stereomers are formed from methyl acrylate and from methyl methacrylate.[3] On the other hand, ethylenes with electron-donor characteristics yield mixtures of 1,2- (1) and 1,3- (2) photocycloadducts with benzene)[1,6,7] endo stereochemistry has been established for the 1,2-adduct of Z-cyclooctene,[9] and the 1,2-adducts of Z-but-2-ene[10] and 2,3-dihydropyran[11] (but see below) have been assigned analogous structures, while the corresponding product from 2,2-dimethyl-1,3-dioxole has been shown to possess the exo configuration.[6] These stereochemical formulations are all in accord with the relative orientations of the addends in the ground-state, as deduced from p.m.r. solvent-shift studies.[12,13] We now report that, contrary to their apparent endo orientations in the ground-state, ethyl vinyl ether, n-butyl vinyl ether, 2,3-dihydropyran, and p-dioxene all give rise to exo 1,2-photocycloadducts with benzene; moreover, with the cyclic vinyl ethers the selectivity of the reaction pathway seems to be dependent upon the ring size.

Irradiation (at 254 nm.) of an equimolar mixture of ethyl vinyl ether and benzene yielded a single 1,2-adduct, together with exo and endo 1,3-products.[14] The 1,2-adduct could be removed quantitatively from the crude mixture by reaction with dienophiles, and for example N-phenyl-maleimide gave a crystalline derivative (3). An exo configuration for the ethoxy group in (3), and hence in the initial 1,2-photocycloadduct (4),[15] was indicated by the p.m.r. spectrum[16] and confirmed by comparison with a sample of (3) prepared from the esterified cyclo-octatetraene-maleic anhydride adduct (8); the reaction sequence involved hydroxymercuration-demercuration to form the hydroxy-diester (9),[18] O-ethylation using ethyl iodide-silver oxide, hydrolysis of the ester groups with aqueous trifluoroacetic acid, thermal conversion of the resulting dicarboxylic acid into the cyclic anhydride, and finally reaction with aniline.

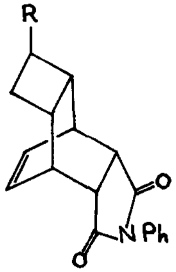
The 1,2-photocycloadduct of n-butyl vinyl ether[14] could similarly be assigned the exo configuration, and these results led to a reconsideration of the analogous 2,3-dihydropyran adduct, previously formulated as an endo compound.[11] It is now evident, from the p.m.r.



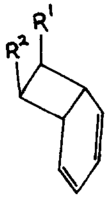
(1)



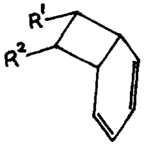
(2)



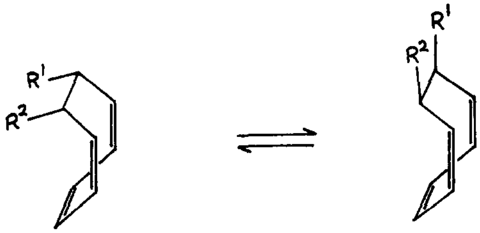
(3) R = OEt



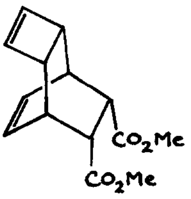
(4) R^1 = OEt
R^2 = H



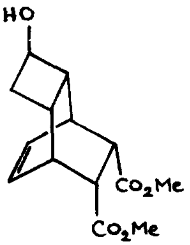
(5) R^1 = OEt, R^2 = H
(7) R^1 = R^2 = $(CH_2)_6$



(6a) (6b)



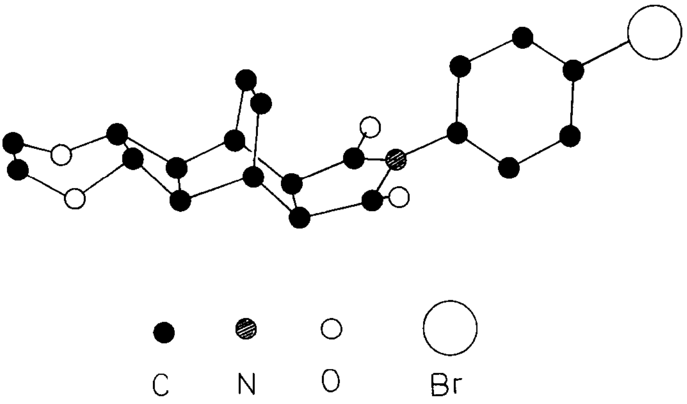
(8)



(9)

spectrum of the *N*-phenylmaleimide derivative, that yet again the stereochemistry is *exo*.

For comparison, we have examined the photocycloaddition of benzene to 2,3-dihydrofuran, 1,3-dioxole, 2-methyl-1,3-dioxole, and p-dioxene. 2,3-Dihydrofuran gave a complex mixture containing at least seven components (contrast 2,3-dihydropyran[11]) ; the dioxoles both yielded mixtures of 1:1 adducts, but under the conditions used the 1,2-cycloadduct was not the major product. A very selective photoreaction was observed with p-dioxene, however, and only the *exo*-1,2-cycloadduct was detected. In this case the stereochemistry was determined by an X-ray crystallographic analysis of the *N*-p-bromophenylmaleimide derivative, which gave the following data: $C_{20}H_{18}NO_4Br$, M = 416.1 , monoclinic, a = 16.687(14), b = 6.359 (8), c = 16.740 (11)Å, β = 90.5 (3)°, V = 1776.3 Å^3, Z = 4, d_m = 1.59, d_c = 1.56, spacegroup I 2 (No.5) ; 501 independent reflections above background were collected on a defractometer and have been refined to R = 0.10. The resulting computed structural diagram for the adduct is given below.



The orientations of the vinyl ethers with respect to benzene, in their loose ground-state associations, may be inferred from p.m.r. spectra as follows. For ethyl vinyl ether,[12] n-butyl vinyl ether, 2,3-dihydropyran,[11] and p-dioxene the vinyl proton resonances were either unaffected by a solvent change from CCl_4 to C_6D_6, or appeared 4-10 Hz downfield, while the methyl and/or methylene signals *all* moved upfield by 10-25 Hz ; this implies an *endo* arrangement of the molecules in the ground-state. In contrast, except for the β-vinyl proton in 2,3-dihydrofuran which showed a zero shift, *all* the signals given by the five-membered ring compounds moved upfield in C_6D_6.[13]

To summarise, the 1,2-photocycloadducts of vinyl ethers with benzene show *exo*-stereochemistry even when the ground-state orientation is *endo*. The selectivity of the addition mode (1,2- or 1,3-) for cyclic vinyl ethers appears to be dependent upon the ring size ; for six-membered ring systems the 1,2-cycloaddition process is efficient and highly selective (contrast cyclohexene[1]).

Acknowledgements

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7. The selectivity of the photoprocess may be predicted from the ionisation potential of the ethylene.[1] With values > *ca*. 9.5 eV, however, modification of the original concept may be required.[8]
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12. D.Bryce-Smith, A.Gilbert, and H.M.Tyrrell, J.C.S.Chem.Comm., 1974, 699.
13. We are grateful to Prof. H.-D.Scharf for providing us with appropriate p.m.r. spectra of 2,2-dimethyl-1,3-dioxole, from which an *exo* orientation of the ground-state molecules could be deduced.
14. The 1,3-adducts will be discussed in a forthcoming paper.
15. In principle, an *endo* compound (5) might equilibrate with the presumably more stable *exo* form (4) *via* the cyclo-octatriene (6). It is evident, however, that the *endo* adduct (7) of *Z*-cyclo-octene[9] retains its integrity.
16. It has been observed that, for structures such as (3), the pattern of the p.m.r. signals due to the two vinylic protons is indicative of the stereochemistry of the group R.[17,18]
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