endo-Selectivity in the Diels–Alder Reactions of Non-conjugated Olefins

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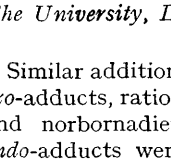
Summary The addition of cyclopentene, *cis*-but-2-ene, and cycloheptene to 2-benzopyran-3-one (**1**) and its 1-methyl derivative gives mainly *endo*-adducts (**2**), and the addition of cyclopentene to (**5**) gives mainly the *cis*-ester (**7**) *via* the *endo*-transition state.

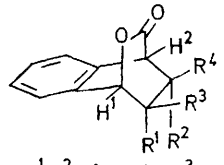
THE preferred formation of *endo*-adducts in the Diels–Alder reactions of unconjugated dienophiles[1] can be taken as evidence for an attractive interaction between the diene and an *endo*-alkyl group.[2] However for the known reactions, steric,[3] torsional, or flexibility[4] factors may also favour *endo*-addition, and the situation is complicated by examples in which either the *endo*- and *exo*-adducts are formed in comparable quantities,[5] or the *exo*-adduct predominates.[6]

To test for favourable diene–*endo*-alkyl group interactions we studied the addition of simple olefins to the *ortho*-quinonoid system (**1**). Here steric factors should be similar for the two transition states. 2-Benzopyran-3-one (**1**) generated by dehydration of *o*-formylphenylacetic acid in acetic anhydride (140°),[7] or benzene containing dicyclohexylcarbodi-imide (80°), reacted with cyclopentene to give the *endo*-adduct (**2**) and the *exo*-adduct (**3**), ratio 6·5 : 1.† The *endo*-adduct was identical to the reduction product (H_2–Pt) of the single adduct obtained from (**1**) and cyclopentadiene. The configuration of the adducts followed from their n.m.r. spectra. For the *endo*-adduct the methylene protons are shielded by the phenylene ring (two 3H multiplets at τ 9·15 and 8·5); for the *exo*-adduct they appear as one multiplet at τ 8·15. For the *endo*-adduct the protons H^1 and H^2 appear as cleanly resolved doublets (J 4·5 and 3 Hz) whilst for the *exo*-adduct this coupling is unresolved as a consequence of the *trans*-periplanar arrangement of the protons H^a and the electronegative lactone unit.[8]

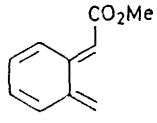
Similar addition of (**1**) to *cis*-but-2-ene gave the *endo*- and *exo*-adducts, ratio 4 : 1, and for the additions of cycloheptene and norbornadiene to 1-methyl-2-benzopyran-3-one the *endo*-adducts were also the major products. These preferred *endo*-additions can either be attributed to attractive diene–alkyl group interactions or possibly to repulsion between the alkyl substituents and the polar lactone unit in the *exo*-transition state. The absence of an impediment



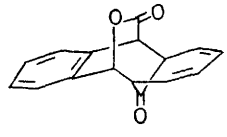
(1)



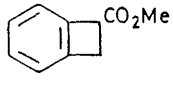
(2) $R^1,R^2 = [CH_2]_3, R^3 = R^4 = H^a$
(3) $R^1 = R^2 = H^a$, $R^3,R^4 = [CH_2]_3$



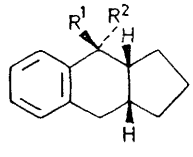
(5)



(4)



(6)



(7) $R^1 = H$, $R^2 = CO_2Me$
(8) $R^1 = CO_2Me$, $R^2 = H$

† *endo-exo*-Ratios were measured for the isolated adducts cleanly separated by short column chromatography (**B.** J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868). The minor adduct was shown to be stable under the conditions of the addition reaction.

to *exo*-addition is shown by the (6 + 4) π-addition of (**1**) to tropone which gives the expected *exo*-adduct (**4**). The first explanation is also favoured by the 3·3 : 1 *endo*–*exo*-ratio observed in the addition of the *ortho*-quinonoid ester (**5**) to cyclopentene. The ester (**5**) was generated by ring opening of the valence-isomer (**6**) at 150°. The *exo*-adduct (**8**) was prepared by hydrogenolysis (H_2/Pd–C/HOAc) of the lactone (**2**) followed by esterification.

The methylene group(s) of cyclopentene and the ester group in (**5**) approach one another in the *endo*-transition state leading to (**7**) but move apart *in* proceeding to (**8**). Accordingly repulsion between these groups should favour the *exo*-adduct. That the *endo*-adduct is still preferred speaks for a small but well defined attractive interaction between an *endo*-alkyl group and the diene system.

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