Diels–Alder Additions with *exo*-Selectivity

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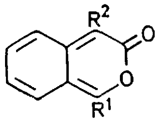
Summary Butadiene, isoprene, cyclopentadiene, dimethyl maleate, norbornadiene, and cyclopentene add to the pyrone (**1**; $R^1 = R^2 = Ph$) to give mostly *exo*-adducts; by comparison with the *exo–endo*-ratios observed for addition to related systems this *exo*-selectivity is attributed to inhibition of secondary interactions by non-planar phenyl substituents.

In trapping 1,4-diphenyl-2,3-naphthoquinone[1] with dienes and olefins we observed predominant formation of *exo*-adducts, and sought precedent for this exceptional Diels–Alder behaviour[2] in additions to the isolable[3] pyrone (**1**; $R^1 = R^2 = Ph$).

With isoprene in benzene at 130° the pyrone (**1**; $R^1 = R^2 = Ph$) gave *exo*-adduct (**2**) (60%) and *endo*-adduct (**3**) (13%). In (**2**) and related *exo*-adducts both the protons H^A are shielded (τ 3·2—3·75), for both phenyl groups can adopt conformations like that shown for one group in (**2**) appropriate for shielding H^A. In the *endo*-adduct (**3**) only one of the protons H^A is shielded since the conformation of the phenyl group shown is destabilised by steric clash with the *endo*-substituent. Chemical evidence for the configurations (**2**) and (**3**) as well as the orientation of addition was obtained by reaction of the adducts with trifluoroacetic acid when (**2**) gave the γ-lactone (**4**) whilst (**3**) gave the indane (**5**). Reaction of (**1**; $R^1 = R^2 = Ph$) with butadiene gave the *exo*-adduct (**6**) (43%) and relatively more *endo*-adduct (**7**) (17%). Preference for *exo*-addition to the diene (**1**; $R^1 = R^2 = Ph$) is associated with the phenyl substituents. Whilst (**1**; $R^1 = R^2 = Ph$) reacts with dimethyl maleate to give more *exo*-adduct (58%) than *endo* (25%), the diene (**1**; $R^1 = Ph$, $R^2 = H$)[4] gives more *endo*-adduct (53%) than *exo* (9%). It is known that (**1**; $R^1 = R^2 = H$) gives only the *endo*-adduct with dimethyl maleate.[4] Phenyl substituents do not significantly inhibit *endo*-addition to the



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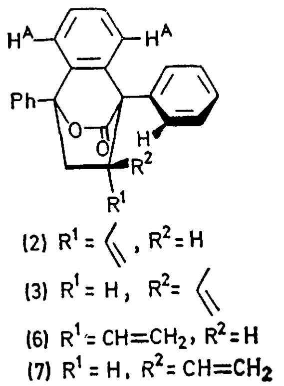

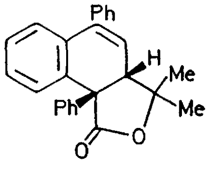

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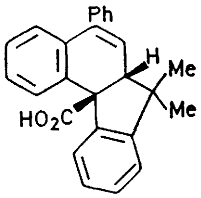

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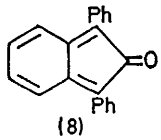

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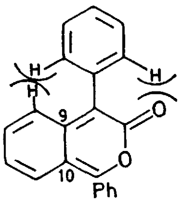

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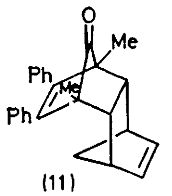

(11)

5-membered ring diene in 1,3-diphenylinden-2-one (**8**)[5]† which gives mainly *endo*-adducts with dimethyl maleate, cyclopentene, and cyclopentadiene. It is likely therefore that the phenyl groups inhibit *endo*-addition by a steric rather than an electronic effect. While the phenyl groups in (**8**) can be coplanar† with the *ortho*-quinonoid system, in (**9**) interactions of the type shown probably prevent full coplanarity. The *ortho*-hydrogens of non-planar phenyl groups will shield C-9 and -10 and so impede the secondary orbital or other interactions which normally favour *endo*-addition.[6] When such interactions are reduced the *exo*-adduct may be favoured by steric effects. In additions to (**1**; $R^1 = R^2 = Ph$) the *exo–endo*-ratio reduces with the effective size of the dienophile. For cyclopentadiene it is 4, for norbornadiene 1·5, and for cyclopropene only the *endo*-adduct is reported.[7] A similar explanation has been proposed for the predominant *exo*-addition of cyclobutenes to 2,5-dimethyl-3,4-diphenylcyclopentadienone (**10**) and the related cyclopentadiene.[8] In agreement we find that addition of the effectively smaller norbornadiene to (**10**) (in refluxing toluene) gives only the *endo*-adduct (**11**).[9] These observations suggest that additions to (**10**) are subject to a measure of steric control. This could account for the preferred formation of *endo*-CO_2Me adducts in the reaction of (**10**) with methyl substituted acrylates[10] which contrasts with the reaction of the same dienophiles with cyclopentadiene, and norbornadiene.[11]

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† *exo*-Addition is more important for 1,3-diphenylbenzo[*c*]furan than for benzo[*c*]furan, suggested incomplete coplanarity of the phenyl groups on this 5-ring diene.

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[4] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 536.

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[6] R. Hoffmann and R. B. Woodward, 'The Conservation of Orbital Symmetry', Verlag Chemie, Weinheim, 1970, p. 145; *endo*-addition of unconjugated olefins is also favoured, D. W. Jones and G. Kneen, preceding communication.

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