Diels–Alder Additions to 1,3-Dimethyldibenz[*e.g.*]inden-2-one

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Summary *endo*-Addition of non-conjugated dienophiles is more important for 1,3-dimethyldibenz[*e.g.*]inden-2-one (**3**) than for the cyclopentadienone (**1**) supporting the view that steric effects associated with non-coplanar phenyl groups in (**1**) impede *endo*-addition.

2,5-Dimethyl-3,4-diphenylcyclopentadienone (**1**) rereacts with cyclopentadiene to give mainly the *endo*-adduct (**2**) but with cyclopentene the *endo* : *oxo* ratio is only 1·27 : 1. This result was interpreted as showing the presence of secondary attractive forces in the *endo*-cyclopentadiene addition and their absence in the *endo*-cyclopentene addition.[1] Another explanation is that the *endo*-transition state is destabilised by a steric effect arising from non-coplanarity of the phenyl groups in (**1**);[2,3] such destabilisation would be greater for the more bulky cyclopentene. To test this hypothesis we have generated the very similar cyclopentadienone (**3**) in which the aryl rings (A) must lie in essentially the same plane as the cyclopentadienone system.

The alcohol (**4**)[4] and acetyl chloride at 0° rapidly precipitate a *cis–trans* mixture (1 : 1) of the chlorides (**5**). This mixture and triethylamine in boiling benzene gave a cyclopentadienone dimer (**6**)† of the usual[5] type. In boiling benzene (**6**) reversibly dissociates to the monomer (**3**) which can be intercepted with *N*-phenylmaleimide to give the adduct (**7**). In contrast to the dissociation of the related dimer of (**1**) no colour accompanies dissociation of (**6**); presumably the equilibrium (**6**) $\rightleftharpoons$ (**3**) more strongly favours the dimeric form.

Dissociation of (**6**) in the presence of cyclopentadiene led to one adduct in 71% recrystallised yield. This is assigned the *endo*-configuration (**8**) since in the presence of Eu(fod)$_3$ the resonance of the olefinic protons is shifted to a much smaller extent than that of the protons H$_a$. Moreover reduction of (**8**) (H$_2$–Pd–C) gave a dihydro-derivative (**9**) in

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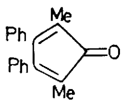
† This dimer was not obtained by the standard acid-catalysed dehydration of the alcohol (**4**) (*cf.* ref. 5).

which the methylene protons appear as two 3H multiplets at τ 9·1 and 8·3, as in similar *endo*-adducts;[6] related *exo*-adducts show one 6H multiplet at τ *ca.* 8·2.

N.m.r. and t.l.c. examination of the adduct fraction obtained from the addition of cyclopentene to (**3**)‡ indicated only one major product, the *endo*-adduct (**9**). It appears therefore that *endo*-addition of cyclopentene to (**1**) is indeed inhibited by non-coplanarity of the phenyl groups for when the steric effect is removed in the addition to (**3**) the normal[7] strong *endo*-selectivity of cyclopentene returns. Similarly in the addition of *cis*-but-2-ene to (**3**) only the *endo*-adduct (**10**) is detected. The addition of (**3**) to *cis*- and *trans*-but-2-ene is stereospecific (n.m.r. comparison of the crude reaction products) in agreement with concerted Diels-Alder addition of (**3**) to these olefins.

The suggestion that non-coplanarity of the phenyl groups in (**1**) favours *exo*-addition was made to account for the *exo*:*endo* ratio of *ca.* 6:1 for the addition of (**1**) to the cyclobutene (**11**).[2] In agreement with a reduced impediment to *endo*-addition in (**3**) we observe an *exo*:*endo* ratio of *ca.* 2:1 for the addition of (**3**) to (**11**). The *exo*-transition state for cyclobutene addition may be favoured by other steric factors; when the steric demands for *exo*- and *endo*-addition are similar, as in the reaction of (**11**) with (**12**), the *endo* adduct predominates (ratio 2—2·5:1) supporting an attractive diene–alkyl group interaction.[6]



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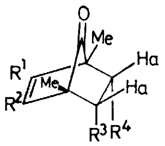
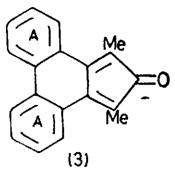




(3)

(2) $R^1 = R^2 = Ph$; $R^3,R^4 = -CH_2CH{=}CH-$

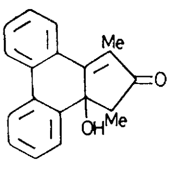
(7) $R^3,R^4 = -CO{\cdot}NPh{\cdot}CO-$

(8) $R^3,R^4 = -CH_2CH{=}CH-$

(9) $R^3,R^4 = [CH_2]_3$

(10) $R^3 = R^4 = Me$

(7)–(10): R^1,R^2 = biphenyl-2,2′-diyl



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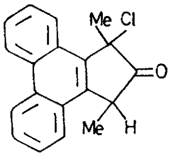

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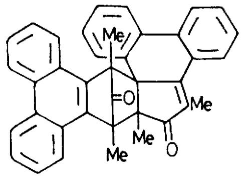

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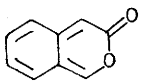

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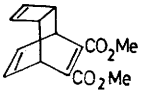

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‡ Addition carried out over 4·5 h in xylene solution in a bomb immersed in an oil-bath at 135—140 °C; almost complete consumption of dimer occurs in 120 h in boiling benzene but the product is contaminated with the cyclopentadiene adduct (**8**).

[1] K. N. Houk, *Tetrahedron Letters*, 1970, 2621.
[2] C. M. Anderson, I. W. McCay, and R. N. Warrener, *Tetrahedron Letters*, 1970, 2735.
[3] D. W. Jones and R. L. Wife, *J.C.S. Chem. Comm.*, 1973, 421.
[4] F. L. C. Baranyovits and J. E. Downes, *B. Pat.* 1,052,951 (*Chem. Abs.*, 1967, **66**, 94727e).
[5] M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261.
[6] *Cf.* D. W. Jones and G. Kneen, *J.C.S. Chem. Comm.*, 1973, 420.
[7] J. G. Martin and R. K. Hill, *Chem. Rev.*, 1961, **61**, 537.