o-Quinonoid Compounds. Part 12.[1] Diels–Alder Additions to 1,3-Dimethylcyclopenta[*l*]phenanthren-2-one

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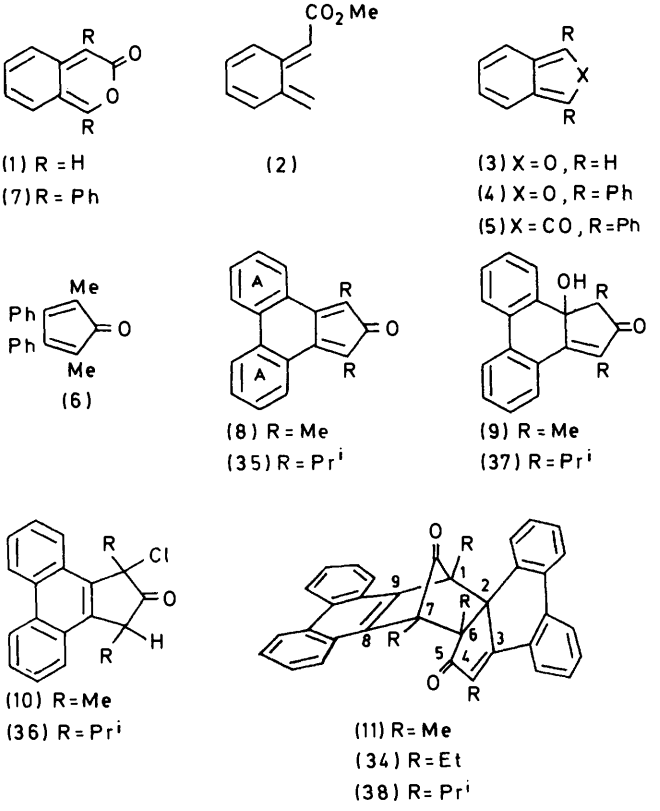
The Diels–Alder dimer (11) of 1,3-dimethylcylcopenta[*l*]phenanthren-2-one (8) is conveniently prepared by dehydrochlorination of 1-chloro-1,3-dimethylcyclopenta[*l*]phenanthren-2-one (10). As judged from trapping experiments with *N*-phenylmaleimide, 1-phenyltriazoline-2,5-dione, and cyclopentadiene the dimer is in rapid equilibrium with the monomer (8) at 20 °C, but no colour accompanies dimer dissociation. *endo*-Addition of non-conjugated dienophiles [cyclopentene, *cis*-but-2-ene, and the cyclobutene (23)] is more important for (8) than for 2,5-dimethyl-3,4-diphenylcyclopentadienone (6), supporting the view that steric effects associated with non-coplanar phenyl groups in (6) impede *endo*-addition. Addition of (8) to tropone gives the *exo*-[6 + 4]π-adduct (21). Either thermolysis or photolysis of (8) affords the formal [4 + 4]π-dimer (32) of 1,3-dimethylcyclopenta[*l*]phenanthren-2-one. 1,3-Diethylcylopenta[*l*]phenanthren-2-one likewise exists as a dissociating [4 + 2]π-dimer (34), but 1,3-di-isopropylcyclopenta[*l*]phenanthren-2-one (35) is a sterically stabilised monomer which shows the same reactivity sequence towards dienophiles as observed for the dimer (11). The unusual n.m.r. spectra of the dimers (11) and (34) are tentatively rationalised in terms of a rapid Cope rearrangement.

We have shown that simple olefins like cyclopentene and *cis*-but-2-ene undergo preferred *endo*-addition to 2-benzopyran-3-one (1) and the *o*-quinodimethane (2).[2] Since steric and torsional effects would be expected to be similar in the *exo*- and *endo*-transition states (TSs) for addition to the pyrone (1), we proposed an attractive diene–alkyl group interaction to explain the observed *endo*-selectivity. Because torsional effects are unequal for *exo*- and *endo*-addition to five-membered ring dienes,[2] such systems are less useful in testing for diene–alkyl group interactions. Nevertheless benzo[*c*]-furan (3),[2] its 1,3-diphenyl derivative (4),[1a,2] and 1,3-diphenylinden-2-one (5) [1a] give mainly *endo*-adducts with cyclopentene. In contrast 2,5-dimethyl-3,4-diphenylcyclopentadienone (6) gives approximately equal quantities of *exo*- and *endo*-adducts with cyclopentene, whereas with cyclopentadiene the dienone (6) gives mainly the *endo*-adduct.[3] This result was interpreted as showing the presence of secondary attractive forces in the cyclopentadiene addition and their absence in the *endo*-cyclopentene addition.[3] The result was moreover generalised to suggest the absence of attractive diene–alkyl group interactions in the Diels–Alder additions of simple olefins. However preferred *exo*-addition of certain cyclobutenes to the dienone (6) had been explained in terms of a steric effect arising from the non-coplanarity of the phenyl groups and the cyclopentadienone ring.[4] Related effects are observed in the Diels–Alder additions of 1,2-diphenylbutadiene [5] and the diphenylpyrone (7).[6] The latter, unlike the unsubstituted pyrone (1), undergoes preferred *exo*-addition of simple olefins.[1a,2] Thus *endo*-TSs for additions to the dienone (6) could be destabilised by a steric effect which would be greater for cyclopentene than cyclopentadiene because of the greater number of out-of-plane hydrogen atoms in the former. To test this idea we sought to generate the very similar cyclopentadienone (8) [1b] in which the aryl rings (A) must lie in essentially the same plane as the cyclopentadienone system. As a dibenz-[*e*,*g*]inden-2-one, compound (8) is a member of the interesting but as yet poorly characterised group of inden-2-ones.[7] Our attempts to prepare (8) were encouraged by the stability of the related 1,3-diphenylcyclopenta[*l*]phenanthren-2-one [8] (phencyclone), and the availability [9] of the alcohol (9) prepared by base-



[1] (*a*) Part 11, D. W. Jones and R. L. Wife, *J.C.S. Perkin I*, 1976, 1654; (*b*) preliminary communication, D. W. Jones, *J.C.S. Chem. Comm.*, 1975, 199.

[2] D. W. Jones and G. Kneen, *J.C.S. Perkin I*, 1976, 1647.

[3] K. N. Houk, *Tetrahedron Letters*, 1970, 2621.

[4] C. M. Anderson, I. W. McCay, and R. N. Warrener, *Tetrahedron Letters*, 1970, 2735; for a related observation see W. G. Dauben, G. T. Rivers, R. J. Tweig, and W. T. Zimmerman, *J. Org. Chem.*, 1976, **41**, 887.

[5] P. C. Jain, Y. N. Mukerjee, and N. Anand, *J. Amer. Chem. Soc.*, 1974, **96**, 2996.

[6] D. W. Jones and R. L. Wife, *J.C.S. Chem. Comm.*, 1973, 421.

[7] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1971, 608; *Chem. Comm.*, 1969, 587.

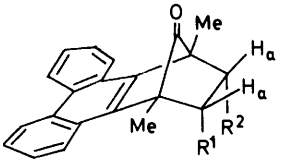
[8] M. A. Ogliaruso, M. G. Romanelli, and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261.

[9] F. L. C. Baranyovits and J. E. Downes, B.P. 1,052,951 (*Chem. Abs.*, 1967, **66**, 94,727e).

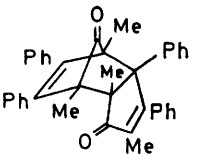
catalysed condensation of phenanthraquinone and diethyl ketone. Attempts to effect acid-catalysed dehydration of the alcohol (9) failed, although the dimer of the dienone (6) and related dimers are readily prepared in this way.[8] Attempted dehydration of the alcohol (9) in boiling acetic anhydride also failed, giving a mixture of rearranged acetates. However the reaction of the alcohol (9) with acetyl chloride led to rapid precipitation of a *cis–trans*-mixture of the rearranged chlorides (10). With triethylamine in boiling benzene this mixture gave the desired cyclopentadienone dimer (11) in good yield. This showed carbonyl bands at 1 769 and 1 688 cm^{-1}, consistent with the presence of a strained carbonyl group and a cyclopentenone, respectively; the unusual n.m.r. spectrum is discussed later.

In chloroform solution at room temperature, the dimer (11) reversibly dissociates to the monomer (8), which can be intercepted with *N*-phenylmaleimide to give the adduct (12). If a large excess of the dienophile is employed the reaction is complete in a few minutes. In contrast, the dimer (13) and a similar excess of *N*-phenylmaleimide undergo half-reaction in *ca.* 20 h. Additions of the monomer (8) to both cyclopentadiene and 4-phenyltriazoline-3,5-dione may also be conducted at room temperature. Unlike the dissociation of the dimer (13) in boiling benzene no colour accompanies dissociation of (11). It is likely therefore that the equilibrium (11) $\rightleftharpoons$ (8) overwhelmingly favours the dimeric form, but that interconversion of (11) and (8) is rapid. Greater Diels–Alder reactivity of (8) than of (6) is in keeping with reduced steric interactions in the *endo*-TS * for the former as well as the higher ground state energy of (8) associated with inden-2-one [7] or 9,10-phenanthroquinodimethane character.[10]

Dissociation of the dimer (11) in the presence of cyclopentadiene led to one adduct (71% recrystallised yield). This is assigned the *endo*-configuration (14) 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 (14) (H_2,Pd–C) gave a dihydro-derivative (15) in which the methylene proton signals appear as two 3 H multiplets at δ 0.9 and 1.7 as in related *endo*-adducts; [2] similar *exo*-adducts show one 6 H multiplet at δ *ca.* 1.8.[2] The alcohol (16) obtained by reduction of (15) with lithium aluminium hydride showed a large shift of the signal due to the protons H_a (*ca.* 3 p.p.m.) and a smaller shift of the methylene proton signal (*ca.* 1 p.p.m.) in the presence of $Eu(fod)_3$. N.m.r. and t.l.c. examination of the adduct fraction from the addition of cyclopentene to (8) † indicated only one major product, the *endo*-adduct (15). It appears therefore that *endo*-addition of cyclopentene to the dienone (6) is indeed inhibited by non-coplanarity of the phenyl groups, for when the steric effect is removed in the addition to (8) the normal strong *endo*-selectivity of cyclopentene [11] returns. Similarly in the addition of *cis*-but-2-ene to (8) only the *endo*-adduct (17) is detected. The *endo*-configuration of this adduct is indicated by the n.m.r. spectrum, which shows that the *endo*-methyl groups are shielded (δ 0.6) in accord with their location over the phenanthrene ring system. In the related *trans*-but-2-ene adduct the *endo*-methyl group is similarly shielded (δ 0.71) but the *exo*-methyl group is not (δ 1.08). The additions of (8) to *cis*- and *trans*-but-2-ene, and to dimethyl maleate and dimethyl fumarate, are highly stereoselective (n.m.r. comparison of the crude products). This observation supports adduct formation by dissociation of the dimer (11) to the monomer (8) followed by concerted Diels–Alder addition to the added olefin.



(12) R^1R^2=CO·NPh·CO
(14) R^1R^2=CH_2·CH:CH
(15) R^1R^2=$[CH_2]_3$
(17) R^1=R^2=Me
(18) R^1=R^2=CO_2Me



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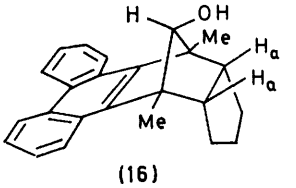

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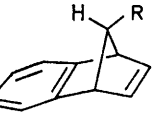

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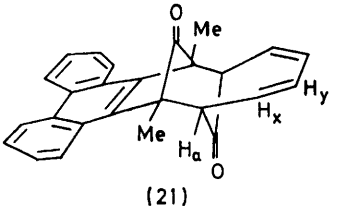

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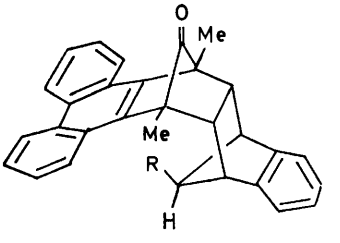

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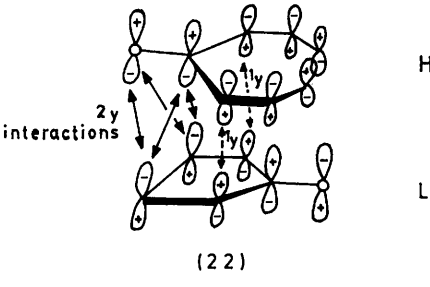


(22)

* The *endo*-configuration of the adduct (12) is assigned on the basis of its n.m.r. spectrum, which shows that the aromatic protons *ortho* to nitrogen are strongly shielded (Experimental section).

† 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 occurred in 120 h in boiling benzene but the product was contaminated with the cyclopentadiene adduct (14).

[10] J. P. Anhalt, E. W. Friend, and E. H. White, *J. Org. Chem.*, 1972, **37**, 1015.
[11] J. G. Martin and R. K. Hill, *Chem. Rev.*, 1961, **61**, 537.

1,4-Dihydro-1,4-methanonaphthalene (19; R = H) adds to (8) to give only the *endo*-adduct (20; R = H), in which the methylene proton directed towards the phenanthrene unit [R in (20)] is more strongly shielded (δ −0.1) than the other methylene proton (δ 0.6). This was established by preparation of the adduct (20; R = D) from the monodeuteriated olefin (19; R = D).[12] The spectrum of (20; R = D) lacked the resonance at δ −0.1 shown by (20; R = H). The phenanthrene unit therefore resembles a phenylene ring in inducing a greater shielding of a *syn*- than of an *anti*-proton. This is in contrast to the effect of a similarly placed double bond or lactone moiety.[2] We have previously pointed out [1] that norbornadiene gives only the *endo*-adduct with the cyclopentadienone (6). This is in accord with a steric impediment in the cyclopentene addition, for the geometry of norbornadiene would be expected to lead to reduced interaction of the dienophile with non-coplanar phenyl rings of the diene.

That *exo*-addition to (8) is not impeded is shown by formation of the *exo*-[6 + 4]π-adduct (21) with tropone. The assigned *exo*-configuration is supported by the chemical shifts of the protons H_a, and H_x and H_y, which correspond closely to the shifts of the analogous protons in the [6 + 4]π-tropone adduct of (6). For the latter the *exo*-configuration was established chemically.[13] Formation of the *exo*-adduct (21) in a case where *endo*-addition is not obstructed by non-coplanar phenyl groups [*cf.* addition of (6)] supports the view that [6 + 4]π-additions take the *exo*-course because of unfavourable secondary interactions in the *endo*-TS.[14] However, as in the addition of tropone to cyclopentadiene,[15] attractive interaction is possible in the *exo*-TS (22) leading to (21).

The suggestion that non-coplanarity of the phenyl groups in the dienone (6) favours *exo*-addition was made to account for the *exo* : *endo* ratio of *ca.* 6 : 1 for the addition of the dienone (6) to the cyclobutene (23).[4] In agreement with a reduced impediment to *endo*-addition in (8) we observe an *exo* : *endo* ratio of *ca.* 2 : 1 for the addition of (8) to (23).* The *exo*-TS for cyclobutene addition may be favoured by other factors; when the steric demands for *exo*- and *endo*-addition are similar, as in the reaction of (23) with 2-benzopyran-3-one (1), the *endo*-adduct predominates (ratio 2—2.5 : 1) supporting an attractive diene–alkyl group interaction.[2]

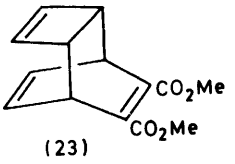
Houk and Luskus [16] have observed a heavy preponderance of the *endo*-CO_2Me adduct in the addition of the dienone (6) to methyl methacrylate (*endo*- : *exo*-CO_2Me ratio 15.7 : 1). This contrasts with the predominance of the *exo*-CO_2Me adduct in the addition of the same dienophile to cyclopentadiene (*endo*- : *exo*-CO_2Me ratio 0.466 : 1).[17] Whereas the latter authors interpret their result in terms of an attractive diene–alkyl group interaction, Houk suggests that the CO_2Me group is ' effectively ' smaller than the methyl group of the dienophile and that steric interaction with a cyclopentadiene methylene hydrogen atom is consequently less in the *exo*- than the *endo*-CO_2Me TS. An alternative explanation for the different selectivities observed for the dienone (6) and cyclopentadiene is that the CO_2Me group is indeed ' effectively ' smaller than the methyl group and that non-coplanarity of the phenyl rings in (6) therefore presents a smaller barrier to *endo*-CO_2Me than to *endo*-Me addition. This is partly true, for addition of methyl methacrylate to (8) gives an *endo*- : *exo*-CO_2Me ratio of *ca.* 6 : 1, to be compared with *ca.* 16 : 1 for methacrylate addition to (6). Kobuke *et al.*[18] have subsequently shown that the homo-Diels–Alder addition of norbornadiene to methyl methacrylate shows a preference for *endo*-Me adduct formation similar to that shown in the cyclopentadiene addition. However in this case the more bulky substituent should prefer the *exo*-position, which, in contrast to the cyclopentadiene addition, is now less hindered [see (26)]. Thus the different selectivities of CO_2Me and Me observed in the addition to the dienone (6) and to cyclopentadiene are probably not entirely due to steric effects. It is possible that the high *endo*-CO_2Me selectivity shown by methacrylate in the additions to (6) and (8) is in part due to a repulsive secondary interaction between the CO_2Me group and the cyclopentadienone carbonyl carbon [see (27)]. Addition of methyl methacrylate to 2-benzopyran-3-one (1) gave the *endo*-CO_2Me adduct (28) and *exo*-CO_2Me adduct (29) in the ratio 2.8 : 1.

The N.m.r. Spectra of the Dimers (11) *and* (34).— Surprisingly, the n.m.r. spectrum of the dimer (11) shows resonances for only two different kinds of methyl group (two 6 H singlets at δ 1.19 and 1.85). In contrast, the related dimer (13) shows distinct peaks for all four methyl groups present (δ 0.59, 1.24, 1.63, and 2.21). As an explanation for this observation the unlikely accidental equivalence of two methyl pairs, *e.g.* 1-Me ≡ 4-Me and 6-Me ≡ 7-Me, was rendered even more unlikely when the related 2,5-diethylcyclopenta[*l*]phenanthren-2-one·dimer was shown to exhibit only two methyl triplets (δ 0.1 and 0.6) and two methylene quartets (δ 1.6 and 2.5). Reference to the boat-like TS (30) for Cope rearrangement of cyclopentadienone dimers shows that C-1 ≡ C-4 and C-6 ≡ C-7. Cope rearrangement will therefore exchange the environments of the 1- and 4-methyl groups as well as the environments of the 6- and 7-methyl groups in (11). This

* On pyrolysis at 180 °C the adducts undergo reverse Diels–Alder reactions to give dimethyl phthalate and the cyclobutenes (24) and (25); the n.m.r. spectra of these products (Experimental section) allow unambiguous assignment of stereochemistry to the original adducts.

[12] W. T. Ford, *J. Org. Chem.*, 1971, **36**, 3979.
[13] R. B. Woodward and K. N. Houk, *J. Amer. Chem. Soc.*, 1970, **93**, 4145.
[14] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970.
[15] W. J. leNoble and B. A. Ojosipe, *J. Amer. Chem. Soc.*, 1975, **97**, 5939.
[16] K. N. Houk and L. J. Luskus, *J. Amer. Chem. Soc.*, 1971, **93**, 4606.
[17] Y. Kobuke, T. Fueno, and J. Furukawa, *J. Amer. Chem. Soc.*, 1970, **92**, 6548.
[18] Y. Kobuke, T. Sugimoto, J. Furukawa, and T. Fueno, *J. Amer. Chem. Soc.*, 1972, **94**, 3633.

explanation is supported by measurement of the n.m.r. spectrum of (11) at −75 °C: the lower field singlet is split into two peaks (δ 1.6 and 2.23) and the higher field singlet is considerably broadened.[19] More rapid rearrangement of (11) than of (13) can be attributed to the rearrangement; Cope rearrangement of hexa-1,5-diene is 41 times faster in the 2-phenyl derivative, 18 times faster in the 3-phenyl derivative, and 2 000 times faster in the 2,5-diphenyl derivative.[20,*] A 1,2,4,5-tetraarylhexa-1,5-diene like (11) would therefore be expected



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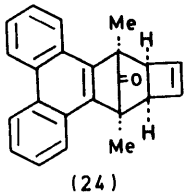

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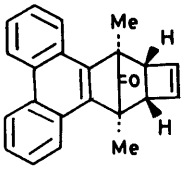

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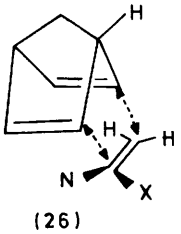

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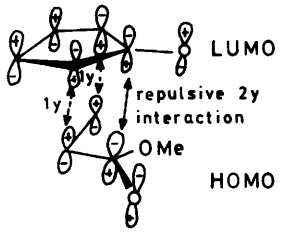

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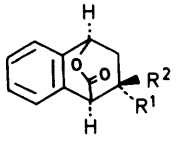
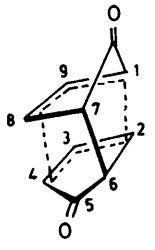


(28) $R^1 = CO_2Me$, $R^2 = Me$
(29) $R^1 = Me$, $R^2 = CO_2Me$



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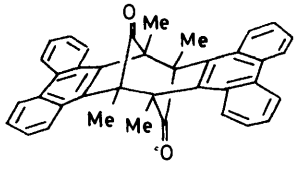
(31)



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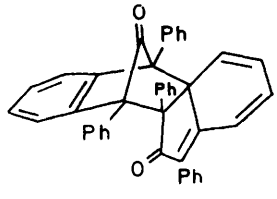

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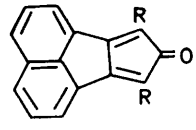

(39)

enforced coplanarity of the aryl groups in (11). A TS of type (30) involving approach of C-4 to C-8 and of C-3 to C-9 will involve smaller steric effects for (11) than for (13). Moreover conjugation of the aryl substituents with the Cope TS will be more effective for (11) than for (13). Such conjugation would be expected to accelerate to rearrange at least 10^4 times more rapidly than the dimer of cyclopentadienone itself. The latter rearranges slowly at 80 °C. It is possible therefore that Cope rearrangement of (11) would be sufficiently rapid to account for the room temperature n.m.r. spectrum. There is little change in the spectrum of (11) between 20 and 105 °C; a rapid monomer–dimer equilibrium could also explain the room temperature spectrum of

* On the basis of these results, Cope rearrangement of 2,5-diphenylhexa-1,5-diyl was suggested to involve a cyclohexane-1,4-diene intermediate (31).[20] However our understanding of substituent effects on sigmatropic processes is poor and it is possible that (31) represents a TS contributor rather than a true intermediate.

[19] B. Fuchs, M. Pasternak, and G. Scharf, *J.C.S. Chem. Comm.*, 1976, 53.
[20] M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, 1973, **95**, 290.

(11) but should lead to a singlet methyl resonance at higher temperature. Attempts to obtain spectra at higher temperatures are complicated by conversion of (11) into a highly insoluble isomer tentatively formulated as (32). This structure is supported by the single carbonyl absorption ($\nu_{max.}$ 1 756 cm^{-1}) shown by the isomer, and by its conversion into the adduct (12) with *N*-phenylmaleimide in boiling *o*-dichlorobenzene. In addition (32) is readily formed by photolysis of (11). Thermal conversion of (11) into (32) involves a 'forbidden' 1,3-shift; this could involve a diradical intermediate formed by homolysis of the 1,2-bond in (11). Alternatively the same diradical could be formed from two molecules of the monomer (8). It is also possible that the 1,3-shift is a concerted-forbidden process which is known to be considerably assisted by a carbonyl group attached to the migrating centre [C-1 in (11)].[21] Generation of 1,3-diphenylinden-2-one (5) [7] at 20 °C gives a formal [4 + 4]π-dimer analogous to (32). Like (32) the dimer of (5) dissociates (at 140 °C), as judged by formation of adducts of the monomer. In view of this resemblance it is tempting to speculate that formation of the [4 + 4]π-dimer of (5) involves transient formation of the Diels–Alder dimer (33), which spontaneously rearranges by a 1,3-shift. The thermal cleavage of the dimer (32) would then involve reversal of the 1,3-shift to give (11) followed by reverse Diels–Alder reaction to afford the monomer (8). The cleavage of the dimer of (5) would follow a similar route. However the possible role of diradicals, *e.g.* that formed by homolysis of the 1,2-bond in (11), in all these processes remains to be delineated.

Diethyl- and Di-isopropylcyclopenta[l]*phenanthren-2-one*.—Doubts regarding intervention of the monomer (8) in the reaction of (11) with olefins are engendered by our failure to observe the colour of the monomer (8) on heating (11) in boiling benzene, toluene, or xylene. We interpret the absence of colour to an equilibrium more strongly favouring the dimeric form (11) than for other cyclopentadienone dimers like (13). This would be in accord with greater steric destabilisation of (13) than of (11) and/or greater electronic destabilisation of (8) than of (6). In an attempt to shift the equilibrium to the monomer side we prepared the diethyl derivative (34) by a slight modification of our route to (11) (see Experimental section). However (34) also showed no colour in boiling xylene. Accordingly we attempted preparation of the di-isopropyl derivative (35). The mixture of chlorides (36) prepared in the usual way * resisted dehydrochlorination with triethylamine in boiling benzene. However smooth dehydrochlorination was effected with diazabicyclononene in benzene at room temperature to give the monomer (35). This showed considerable reactivity towards oxygen when in solution, but was fairly stable as the green-black crystalline solid. It showed carbonyl absorption at 1 683 cm^{-1} and u.v. bands [$\lambda_{max.}$ (CH_2Cl_2) 570, 340, 329, and 287 nm] similar to those of phencyclone [$\lambda_{max.}$ (CH_2Cl_2) 625, 362, and 298 nm] but with the expected shift to lower wavelengths. The n.m.r. spectrum of (35) did not reveal the presence of the dimer (38). The isolation of this compound lends support to our view that the monomer (8) is involved in the reaction of the dimer (11) with olefins. Moreover the reaction of the dimer (11) with *N*-phenylmaleimide is more rapid than its reaction with dimethyl fumarate, which is in turn more rapid than its reaction with dimethyl maleate. The reactivity of (35) towards these dienophiles follows precisely the same order. The phenanthrocyclopentadienone system resembles the acenaphthylenocyclopentadienone system (39).[22] In both systems the monomer is predominant when R = Ph or Pr^i but the dimer is predominant when R = Me or Et. However for the dimers of (39; R = Me or Et) the colour of the monomers is clearly observed in hot benzene. The Diels–Alder reactions of phencyclone have been investigated in some detail.[23]

* The reaction of phenanthraquinone with di-isobutyl ketone proceeded poorly and the alcohol (37) required chromatographic isolation (see Experimental section).

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified i.r. spectra refer to Nujol mulls, and n.m.r. spectra to solutions in deuteriochloroform measured with a Perkin-Elmer R 12 spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light petroleum (b.p. 60—80 °C) and chromatography on silica to short-column chromatography [24] over Kieselgel G (Merck).

3,3a-*Dihydro*-3a-*hydroxy*-1,3-*dimethylcyclopenta*[l]*phenanthren-2-one* (9).—Methanol (80 ml), phenanthraquinone (40 g), pentan-3-one (24 g), and potassium hydroxide (2.4 g) were stirred at 20 °C (24 h). The product was diluted with water, made acidic with 2N-sulphuric acid, and extracted with dichloromethane. The organic extract was washed with water, dried ($MgSO_4$), and evaporated to give the crude hydroxy-ketone (9), which was purified by crystallisation from the minimum quantity of benzene and washed on the filter with a little *cold* benzene to remove almost all the brown colour. The product (31 g) had m.p. 150° (lit.,[9] 154°), $\nu_{max.}$ 3 375, 1 685, 1 638, and 1 604 cm^{-1}, δ 1.47 (3 H, d, *J* 7 Hz), 2.0 (3 H, s), 2.2br (1 H, s, exch. D_2O), 2.95 (1 H, q, *J* 7 Hz), and 7.2—8.0 (8 H, m). The reaction may be conducted on a steam-bath (3 h) without noticeable loss of yield.

1-*Chloro*-1,3-*dimethylcyclopenta*[l]*phenanthren-2-one* (10).—The foregoing hydroxy-ketone (31 g) was treated with acetyl chloride (96 ml) with gentle swirling. After some gas evolution the mixture was stirred at 0—5 °C (1 h). The white precipitate was filtered off and washed with petroleum to give *compound* (10) as a *ca.* 1 : 1 mixture of stereoisomers (27 g), m.p. 140—145° (Found: M^+, 294.0811 and 296.0774. $C_{19}H_{15}{}^{35}ClO$ requires *M*, 294.0811. $C_{19}H_{15}{}^{37}ClO$ requires *M*, 296.0782), $\nu_{max.}$ 1 764 cm^{-1}, δ 1.63 (3 H, d, *J* 7 Hz), 1.76 (3 H, d, *J* 7 Hz), 2.19 (3 H, s), 2.22 (3 H,

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s), 4.05 (2 H, m, overlapping 1 H quartets, *J* 7 Hz), 7.4—8.0 (8 H, m), and 8.3—8.85 (4 H, m).

The Dimer (11) *of* 1,3-*Dimethylcyclopenta*[l]*phenanthren*-2-*one*.—A mixture of the stereoisomeric chlorides (10) (27 g) in benzene (200 ml) was added over 5—10 min to triethylamine (18.54 g) in boiling benzene (50 ml). After boiling under reflux (1 h) the product was washed with water, and filtered to remove the *dimer* (11) (14.8 g). The filtrate was diluted with methylene chloride and washed with 2N-sulphuric acid and water, dried ($MgSO_4$), and evaporated. Crystallisation of the residue from benzene gave more (6.7 g) of the dimer (11), m.p. 314—316° (decomp. to a red melt) (from benzene) (Found: C, 88.45; H, 5.45. $C_{38}H_{28}O_2$ requires C, 88.3; H, 5.5%), $\nu_{max.}$ 1 769, 1 688, and 1 628 cm^{-1}; δ 1.19 (6 H, s, 2 × Me), 1.85 (6 H, s, 2 × Me), 6.7—8.0 (12 H, m), and 8.15—8.5 (4 H, m).

Additions to 1,3-*Dimethylcyclopenta*[l]*phenanthren*-2-*one*.—(*a*) *N*-Phenylmaleimide (44 mg), the dimer (11) (65 mg), and benzene (4 ml) were boiled under reflux (3 h). Precipitation began after about 15 min. The product was diluted with dichloromethane and filtered to remove a trace of insoluble material. Evaporation of the filtrate and crystallisation of the residue from ethanol gave the *adduct* (12) (110 mg), m.p. 254—257° (Found: C, 80.9; H, 4.9; N, 3.35. $C_{29}H_{21}NO_3$ requires C, 80.7; H, 4.9; N, 3.25%), $\nu_{max.}$ 1 720, 1 780, and 1 800 cm^{-1}, δ 2.24 (6 H, s, 2 × Me), 3.37 (2 H, s, methine), 5.7—5.92 (2 H, m, aromatic), 6.72—7.05 (3 H, m, aromatic), 7.43—7.75 (4 H, m, aromatic), 8.22—8.42 (2 H, m, aromatic), and 8.58—8.8 (2 H, m, aromatic). This adduct was also formed at room temperature (18 h). The dimer (11) (40 mg) and *N*-phenylmaleimide (250 mg) in deuteriochloroform (*ca.* 0.5 ml) were converted into the adduct (12) in *ca.* 5 min (n.m.r.).

(*b*) Cyclopentadiene (2 ml), the dimer (11) (0.5 g), and benzene (20 ml) were boiled under reflux (2.5 h). Evaporation in a high vacuum on a water-bath gave the *adduct* (14) (0.45 g), m.p. 181—183° (from chloroform–ethanol) (Found: C, 88.95; H, 6.45%; M^+, 324.1507. $C_{24}H_{20}O$ requires C, 88.85; H, 6.2%; *M*, 324.1514), δ 1.9 (1 H, dm, *J* 19 Hz, CH_2), 1.96 (3 H, s), 2.01 (3 H, s), 2.45 (1 H, d, *J* 19 Hz, CH_2), 2.8 (1 H, td, *J* 7.5 and 4 Hz, methine), 3.35 (1 H, dm, *J* 7.5 Hz, allylic methine), 4.9—5.4 (2 H, m, olefinic), 7.32—7.7 (4 H, m), 8.0—8.42 (2 H, m), and 8.5—8.82 (2 H, m). In the presence of $Eu(fod)_3$ the methine signals underwent downfield shifts (0.75 p.p.m.) comparable to those of the methyl groups (0.60 p.p.m.); the olefinic proton signals showed a smaller shift (0.25 p.p.m.).

Reduction of this product with hydrogen over Adams catalyst in the usual way in ethyl acetate as solvent gave a product identical (i.r. and n.m.r. spectra) with the cyclopentene adduct described below.

(*c*) Cyclopentene (1.5 ml), the dimer (11) (200 mg), and xylene (4.5 ml) were heated in a stainless steel bomb immersed in an oil-bath at 135—140 °C (4.5 h). The product was evaporated to dryness; the n.m.r. spectrum of the methylene-chloride-soluble portion (153 mg) exhibited only one strong methyl resonance. The *adduct* (15) crystallised from petroleum; m.p. 168—172° (Found: C, 88.55; H, 6.75. $C_{24}H_{22}O$ requires C, 88.3; H, 6.8%), $\nu_{max.}$ 1 780 cm^{-1}, δ 0.9 (3 H, m), 1.7 (3 H, m), 1.95 (3 H, s), 2.54 (2 H, m), 7.55 (4 H, m), 8.3 (2 H, m), and 8.71 (2 H, m). When this reaction was conducted in boiling benzene over 5 days the n.m.r. spectrum of the crude product indicated the presence of the cyclopentadiene adduct (14) (10—20%) as well as the expected cyclopentene adduct; reduction of the crude product with hydrogen over 10% palladium–charcoal in ethyl acetate gave the pure cyclopentene adduct.

Reduction of the cyclopentene adduct (100 mg) with lithium aluminium hydride (40 mg) in boiling ether (7 ml) (1 h), and work-up by dropwise addition of water, filtration, drying ($MgSO_4$), and evaporation of the filtrate gave the *alcohol* (16) (100 mg), m.p. 242—244° (from benzene–petroleum) (Found: C, 87.55; H, 7.45. $C_{24}H_{24}O$ requires C, 87.8; H, 7.4%), $\nu_{max.}$ 3 620 cm^{-1}, δ 0.7—1.6 (6 H, m, CH_2), 1.83 (6 H, s), 2.0br (1 H, s, OH), 2.85 (2 H, m, methine), 3.2 (1 H, s, C*H*OH), 7.25—7.7 (4 H, m), 8.3—8.52 (2 H, m), and 8.6—8.85 (2 H, m). In the presence of $Eu(fod)_3$ the methylene signals undergo a smaller downfield shift (*ca.* 1 p.p.m.) than those of the ring-junction methine protons (*ca.* 3 p.p.m.), the methyl groups (*ca.* 2 p.p.m.) and *H*COH (*ca.* 5 p.p.m.).

(*d*) *cis*-But-2-ene (2.5 ml; condensed at −78 °C), the dimer (11) (150 mg), and xylene (4.5 ml) were heated in a steel bomb immersed in an oil-bath at 140 °C (5 h). The product was filtered to remove the insoluble dimer (32) (60 mg), and the filtrate evaporated to dryness in high vacuum at 100 °C. The n.m.r. spectrum of the crude product (80 mg) indicated the presence of only one adduct. Crystallisation from petroleum containing a little benzene gave the cis,endo-*adduct* (17), m.p. 209—211° (Found: C, 87.6; H, 7.0. $C_{23}H_{22}O$ requires C, 87.9; H, 7.0%), δ 0.6 (6 H, 4 lines, $X_3X'_3$ part of $X_3AA'X'_3$, separation of outer lines 6.5 Hz, 2 × CH_3), 1.85 (6 H, s), 2.3 (2 H, m, AA′ part, methine), 7.5 (4 H, m), 8.18 (2 H, m), and 8.65 (2 H, m).

(*e*) *trans*-But-2-ene (2 ml), the dimer (11) (150 mg), and xylene (4 ml) were heated in a bomb immersed in an oil-bath at 150 °C (5 h). Work-up as in (*d*) gave the dimer (32) (100 mg) and the trans-*adduct* (50 mg), m.p. 169—171° (from petroleum) (Found: C, 88.0; H, 7.05%), δ 0.71 (3 H, d, *J* 6 Hz), 1.08 (3 H, d, *J* 5 Hz), 1.2—1.75 (2 H, m, methine), 1.84 (3 H, s), 1.90 (3 H, s), 7.57 (4 H, m), 8.26 (2 H, m), and 8.74 (2 H, m).

(*f*) Methyl methacrylate (1.0 ml), the dimer (11) (150 mg), and toluene (5 ml) were boiled under reflux (4 h). Evaporation gave a product (170 mg) which was chromatographed on silica in benzene–ether (49 : 1) to give first the endo-*methoxycarbonyl adduct* (120 mg), m.p. 118—119° (from benzene–petroleum) (Found: C, 80.0; H, 6.3. $C_{24}H_{22}O_3$ requires C, 80.4; H, 6.2%), δ 1.4 (3 H, s), 1.61 (1 H, d, *J* 12 Hz, CH_2), 1.99 (3 H, s), 2.06 (3 H, s), 2.77 (1 H, d, *J* 12 Hz, CH_2), 3.1 (3 H, s, OMe), 7.55 (4 H, m), 8.28 (2 H, m), and 8.69 (2 H, m). Continued elution gave the exo-*methoxycarbonyl adduct* (20 mg), m.p. 236—238° (from benzene–petroleum) (Found: C, 80.6; H, 6.3%), δ 0.9 (3 H, s), 1.5 (1 H, d, *J* 12 Hz, CH_2), 1.82 (3 H, s), 2.03 (3 H, s), 2.65 (1 H, d, *J* 12 Hz, CH_2), 3.75 (3 H, s, OMe), 7.62 (4 H, m), 8.2 (2 H, m), and 8.76 (2 H, m).

(*g*) The cyclobutene (23) (500 mg), the dimer (11) (100 mg), and toluene (5 ml) were boiled under reflux (6 h). The crude product was evaporated at 100 °C in a high vacuum and chromatographed on silica in benzene–ether (49 : 1). Elution with the same solvent gave first a fraction (40 mg) rich in the *endo*-adduct (*endo–exo* ratio 2 : 1 by n.m.r.), followed by a fraction (25 mg) rich in the *exo*-adduct (*exo–endo* ratio 2 : 1 by n.m.r.), and finally the *exo*-adduct (50 mg), δ 1.76br (2 H, s), 1.94 (6 H, s), 2.13br (2 H, s), 3.75 (6 H, s), 4.05br (2 H, s), 6.31 (2 H, t, *J* 3 Hz), 7.52 (4 H, m), 8.22 (2 H, m), and 8.68 (2 H, m), $\nu_{max.}$ 1 780, 1 735, 1 720, 1 640, 1 610, and 1 575 cm^{-1}. Comparisons among the n.m.r. spectra indicated that the *endo*-adduct

had the following resonances: δ 1.45br (2 H, s), 1.95 (6 H, s), 2.1br (2 H, s), 3.57 (6 H, s), *ca.* 4br (2 H, s), 6.6 (2 H, t, *J* 3 Hz), 7.61 (4 H, m), 8.3 (2 H, m), and 8.8 (2 H, m). The first and third fractions were separately heated in an oil-bath (180 °C; 15 min). In each case the product was purified by chromatography on silica in benzene. The first fraction gave mainly the endo-*cyclobutadiene adduct* (25), m.p. 153—155 and 165° (from benzene–petroleum) (Found: C, 89.2; H, 5.65. $C_{23}H_{18}O$ requires C, 89.0; H, 5.85%), δ 2.01 (6 H, s), 3.1 (2 H, s), 5.41 (2 H, s), 7.56 (4 H, m), 8.25 (2 H, m), and 8.72 (2 H, m). The third fraction gave the exo-*cyclobutadiene adduct* (24), m.p. 224—225° (from benzene–petroleum) (Found: C, 89.0; H, 5.9%), δ 1.95 (6 H, s), 3.0 (2 H, s), 6.52 (2 H, s), 7.60 (4 H, m), 8.3 (2 H, m), and 8.75 (2 H, m).

(*h*) Tropone (212 mg), the dimer (11) (258 mg), and tetrahydrofuran (5 ml) were boiled under reflux (18 h). The solvent was evaporated off and the residue diluted with benzene (5 ml) and boiled under reflux (8 h). The filtered solution deposited the *adduct* (21) (150 mg), m.p. 308—310° (decomp. to a red melt) (Found: C, 86.0; H, 5.75. $C_{26}H_{20}O_2$ requires C, 85.7; H, 5.5%), $\nu_{max.}$ 1 730 and 1 769 cm^{-1}, δ 1.85 (6 H, s), 3.68 (2 H, m), *ca.* 5.9 (4 H, m), 7.55 (4 H, m), 8.2 (2 H, m), and 8.7 (2 H, m). The filtrate, diluted with petroleum, deposited a mixture (80 mg) of the dimer (11) and the adduct (21).

(*i*) 1,4-Dihydro-1,4-methanonaphthalene (200 mg), the dimer (11) (100 mg), and toluene (3 ml) were boiled under reflux (8 h). The cooled product was filtered to remove the dimer (32) (20 mg), the filtrate evaporated, and the residue crystallised from methanol to give the *adduct* (20; R = H) (70 mg), m.p. 254—256° (Found: C, 89.95; H, 5.9. $C_{30}H_{24}O$ requires C, 90.0; H, 6.0%), $\nu_{max.}$ 1 766 cm^{-1}, δ −0.1br (1 H, d, *J* 10 Hz, CH_2), 0.6br (1 H, d, *J* 10 Hz, CH_2), 2.06 (6 H, s), 2.13 (2 H, s), 3.21br (2 H, s), 7.01 (4 H, m), 7.61 (4 H, m), 8.43 (2 H, m), and 8.78 (2 H, m). The experiment was repeated with 1,4-dihydro-1,4-methanonaphthalene specifically labelled with deuterium in the 9-*anti*-position and the labelled *adduct* (20; R = D) was isolated as before; m.p. 253—255° (from chloroform–methanol) (Found: C, 89.5; H, 6.3. $C_{30}H_{23}DO$ requires C, 89.8; H, 6.2%). The n.m.r. spectrum differed from that of (20; R = H) in that the doublet at δ −0.1 was absent, and the doublet at δ 0.6 had become a singlet.

(*j*) Dimethyl maleate (130 mg), the dimer (11) (52 mg), and benzene (3 ml) were boiled under reflux (18 h). Evaporation in high vacuum at 100 °C and chromatography on silica in benzene–ether (9 : 1) gave first a fraction (13 mg) which was examined by n.m.r. but was otherwise uncharacterised, and then the *maleate adduct* (18) (53 mg), m.p. 244—246° (from chloroform–ethanol) (Found: C, 74.75; H, 5.7%; M^+, 402.146. $C_{25}H_{22}O_5$ requires C, 74.6; H, 5.5%; *M*, 402.147), δ 2.1 (6 H, s), 3.29 (6 H, s), 3.43 (2 H, s), 7.6 (4 H, m), 8.38 (2 H, m), and 8.73 (2 H, m). Comparison of the n.m.r. spectrum of the crude product with that of the fumarate adduct described below indicated the presence of less than 3% of the fumarate adduct.

(*k*) Dimethyl fumarate (120 mg), the dimer (11) (52 mg), and benzene (3 ml) were boiled under reflux (6 h). Work-up and chromatography as in (*j*) gave the *fumarate adduct* (76 mg), m.p. 214—217° (from chloroform–ethanol), (Found: C, 74.15; H, 5.35%; M^+, 402.147), δ 1.92 (3 H, s), 2.21 (3 H, s), 3.22 (1 H, d, *J* 5.5 Hz), 3.25 (3 H, s), 3.51 (1 H, d, *J* 5.5 Hz), 3.74 (3 H, s), 7.54 (4 H, m), 8.28 (2 H, m), and 8.66 (2 H, m).

(*l*) 4-Phenyltriazoline-3,5-dione (35 mg) and the dimer (11) (52 mg) were kept in benzene (3 ml) for 18 h. Evaporation and crystallisation of the residue from chloroform–ethanol gave the *adduct* (61 mg), m.p. 218—220° (Found: C, 74.65; H, 4.4; N, 9.35. $C_{27}H_{19}N_3O_3$ requires C, 74.8; H, 4.4; N, 9.7%), $\nu_{max.}$ 1 815, 1 780, 1 730, 1 615, and 1 605 cm^{-1}, δ 2.55 (6 H, s), 6.7 (2 H, m), 7.1 (3 H, m), 7.67 (4 H, m), 8.45 (2 H, m), and 8.68 (2 H, m).

Additions to 2-Benzopyran-3-one.—(*a*) *o*-Formylphenylacetic acid (80 mg), acetic anhydride (5 ml), and methyl methacrylate (1 ml) were boiled under reflux (1 h). Evaporation under reduced pressure on a water-bath and chromatography on silica in benzene–ether (9 : 1) gave first the endo-*methoxycarbonyl adduct* (28) (84 mg) as an oil (Found: M^+, 246.0891. $C_{14}H_{14}O_4$ requires *M*, 246.0892), δ 1.5 (3 H, s), 2.09 (1 H, dd, *J* 14 and 4 Hz, CH_2), 2.66 (1 H, dd, *J* 14 and 2 Hz, CH_2), 3.46 (3 H, s, OMe), 4.05 (1 H, s), 5.52 (1 H, dd, *J* 4 and 2 Hz), and 7.2 (4 H, aromatic). Continued elution gave the exo-*methoxycarbonyl adduct* (29) (30 mg) (Found: M^+, 246.0888), δ 0.99 (3 H, s), 1.5 (1 H, d, *J* 14 Hz, CH_2), 3.19 (1 H, dd, *J* 14 and 4 Hz, CH_2), 3.82 (3 H, s, OMe), 4.01 (1 H, s), 5.61br (1 H, d, *J* 4 Hz), and 7.39 (4 H, aromatic). The mass spectra of both adducts show strong peaks at *m/e* 202 ($M - CO_2$), 143 ($M - CO_2 - CO_2Me$), 142 ($M - CO_2 - CO_2Me - H$), and 128 ($M - CO_2 - CO_2Me - Me$), as well as at *m/e* 146 (*M* − dienophile) and 118 (*M* − dienophile − CO).

(*b*) The cyclobutene (23) (246 mg), *o*-formylphenylacetic acid (82 mg), and acetic anhydride (5 ml) were boiled under reflux (70 min). The product was evaporated under reduced pressure on a water-bath, and the residue crystallised from ethanol to give the endo-*adduct* (55 mg), m.p. 180—197° (decomp.) (Found: C, 70.8; H, 5.15. $C_{23}H_{20}O_6$ requires C, 70.4; H, 5.1%), δ 1.36 (2 H, m, cyclobutane CH), 2.25br (2 H, m, cyclobutane CH), 3.61 (6 H, s, OMe), 3.85 (1 H, d, *J* 4 Hz, HC·CO), 3.75—4.2 and partly overlapping the preceding signal (2 H, m, bis-allylic CH), 5.46 (1 H, d, *J* 5 Hz, HCOCO), 6.52 (2 H, t, *J* 4 Hz, olefinic), and 7.28 (4 H, aromatic).

The mother-liquor was chromatographed on silica in benzene–ether (9 : 1). This gave a fraction (84 mg) rich in the *exo*-isomer which crystallised from a *little* methanol to give the exo-*adduct* (25 mg), m.p. 180—184° (Found: C, 70.9; H, 5.3%), δ 1.8br (2 H, s, cyclobutane CH), 2.1—2.78 (2 H, m, cyclobutane CH), 3.75 (6 H, s, OMe), 3.86—4.3 (3 H, m, overlapping HCCO and bisallylic CH), 5.5br (1 H, s, HCOCO), 6.42 (2 H, t, *J* 3.5 Hz, olefinic), and 7.25 (4 H, aromatic).

The *endo–exo*-ratio was determined by heating *o*-formylphenylacetic acid (160 mg), the cyclobutene (23) (125 mg), and acetic anhydride (4 ml) as above (1.5 h). The product was evaporated at 100 °C in high vacuum and chromatographed on silica in benzene–ether (9 : 1). The fraction containing the *endo-* and *exo*-adducts was examined by n.m.r., which indicated an *endo–exo* ratio of 2 : 1.

The Dimer (32).—The dimer (11) (150 mg) in toluene (5 ml) was boiled under reflux (18 h). Filtration gave the *dimer* (32) (90 mg), m.p. 314—316° (decomp. to a red melt) (Found: M^+, 516.2075. $C_{38}H_{28}O_2$ requires *M*, 516.2089), $\nu_{max.}$ 1 756 cm^{-1}. Its extreme insolubility prevented determination of its n.m.r. spectrum. The mass spectrum showed a strong *M*/2 peak (100%) as well as peaks of *m/e* 230 (77%), 229 (70.3), 228 (46.9), 227 (18.7), 226 (20.8), and 215 (93.8).

The dimer (32) (40 mg) and *N*-phenylmaleimide (100 mg)

in *o*-dichlorobenzene (2 ml) were boiled under reflux (1 h). Evaporation under high vacuum at 100 °C and crystallisation of the residue from ethanol gave the adduct (12) (62 mg), identical (i.r. and n.m.r. spectra) with the product previously prepared.

1,3-*Diethyl*-3,3a-*dihydro*-3a-*hydroxycyclopenta*[l]*phenanthren*-2-*one*.—Methanol (40 ml), phenanthraquinone (5 g), heptan-4-one (5.5 g), and potassium hydroxide (2.5 g) in methanol (8 ml) were stirred at 20 °C. After *ca.* 30 min the quinone went into solution, the colour lightened, and the alcohol began to precipitate after *ca.* 1 h. After 4 h the product was filtered off and washed with water and a little cold methanol to give the *hydroxy-ketone* (2.41 g), m.p. 142—145° (from methanol) (Found: C, 83.0; H, 6.45. $C_{21}H_{20}O_2$ requires C, 82.9; H, 6.6%), $\nu_{max.}$ 3 470, 1 678, and 1 643 cm^{-1}, δ 1.1 (3 H, t, *J* 7 Hz), 1.29 (3 H, t, *J* 7 Hz), 1.9 (2 H, quint, *J* 7 Hz), 2.27 (1 H, s, exch. D_2O, OH), 2.40 (2 H, q, *J* 7 Hz), 2.8 (1 H, t, *J* 6.5 Hz), and 7.1—8.3 (8H, m, aromatic).

The Dimers of 1,3-*Diethylcyclopenta*[l]*phenanthren*-2-*one*.—The foregoing alcohol (1.25 g) and acetyl chloride (4 ml) were stirred at room temperature (2 h). The crude product was evaporated under reduced pressure at 20 °C and the resulting gum boiled with triethylamine (1 g) in benzene (5 ml) (2 h). The product was diluted with benzene, shaken with water, and filtered to remove the supposed [4 + 4]π-dimer (110 mg), $\nu_{max.}$ 1 758 cm^{-1}. The filtrate was washed with 2N-hydrochloric acid and water, dried ($MgSO_4$), and evaporated; the residue crystallised from $CHCl_3$–EtOH to give the *Diels–Alder dimer* (34) (520 mg), m.p. 287—288° (decomp.) (Found: C, 87.85; H, 6.3. $C_{42}H_{36}O_2$ requires C, 88.1; H, 6.3%), $\nu_{max.}$ 1 765 and 1 693 cm^{-1}, δ (90 MHz) 0.1 (6 H, t, *J* 7.5 Hz), 0.6 (6 H, t, *J* 7.5 Hz), 1.6 (4 H, q, *J* 7.5 Hz), 2.5 (4 H, q, *J* 7.5 Hz), and 6.7—8.5 (16 H, m, aromatic).

1,3-*Di-isopropylcyclopenta*[l]*phenanthren*-2-*one*.— 2,6-Dimethylheptan-4-one (6 g), phenanthraquinone (5 g), and potassium hydroxide (3.5 g) in methanol (48 ml) were stirred at 20 °C (24 h). The product was filtered to remove unchanged quinone (2.7 g), and evaporated under reduced pressure. The crude product (2.7 g) was chromatographed on silica in benzene–ether (97 : 3) to give 3,3a-*dihydro*-3a-*hydroxy*-1,3-*di-isopropylcyclopenta*[l]*phenanthren*-2-*one* (335 mg), m.p. 160—163° (from methylene chloride–petroleum) (Found: C, 83.05; H, 6.95. $C_{23}H_{24}O_2$ requires C, 83.1; H, 7.3%), $\nu_{max.}$ 3 470s, 3 570 and 3 600w, 1 695, and 1 633 cm^{-1}, δ 1.15 (6 H, d, *J* 6.5 Hz), 1.39 (6 H, d, *J* 6.5 Hz), 2.0 (1 H, exch. D_2O, OH), 2.5 (1 H, m), 2.96 (1 H, d, *J* 3 Hz), 3.1 (1 H, m), and 7.3—8.1 (8 H, m, aromatic). This alcohol (55 mg) and acetyl chloride (*ca.* 2 ml) were stirred at 20 °C (2 h), and the crude product evaporated at 20 °C under reduced pressure. It was then taken up in benzene (4 ml), 1,5-diazabicyclo[4.3.0]non-5-ene (400 mg) was added, and the mixture was stirred under nitrogen (2 h). The product was diluted with methylene chloride and washed with 2N-hydrochloric acid, dried ($MgSO_4$), and evaporated to give a green-black crystalline solid (*ca.* 40 mg). Rapid crystallisation by precipitation from methylene chloride with ethanol gave 1,3-*di-isopropylcyclopenta*[l]*phenanthren*-2-*one* (35) as stout needles, m.p. 190—195° (decomp.) (Found: M^+, 314.1660. $C_{23}H_{22}O$ requires *M*, 314.1670), $\nu_{max.}$ 1 683 cm^{-1}, δ 1.31 (12 H, d, *J* 7 Hz), 3.16 (2 H, m, *J* 7 Hz), and 7—7.9 (8 H, m, aromatic), $\lambda_{max.}$ 570, 340, 329, 287, and 275 nm. The rapid deterioration of the sample in dilute solution precluded determination of ε values. The strong peak at 287 nm had disappeared completely after 30 min. Apart from the molecular ion (100%) the mass spectrum included strong peaks at *m/e* 286 (18%), 271 (38.8), 256 (22), 244 (55.6), 243 (36.8), and 239 (24.5).

Diels–Alder Additions to 1,3-*Di-isopropylcyclopenta*[l]*phenanthren*-2-*one*.—The diene was used in freshly prepared crude form for the following additions. The crude dienone (*ca.* 40 mg) in benzene (4 ml) was treated with *N*-phenylmaleimide (50 mg). Gentle warming on a water-bath (*ca.* 30 s) led to complete loss of colour, and crystallisation of the product from ethanol gave the N-*phenylmaleimide adduct* (30 mg), m.p. 266—267° (Found: C, 81.0; H, 5.9; N, 2.6%; M^+, 487.215. $C_{33}H_{29}NO_3$ requires C, 81.3; H, 6.0; N, 2.9%; *M*, 487.215), $\nu_{max.}$ 1 808, 1 788, and 1 733 cm^{-1}, δ 1.29 (6 H, d, *J* 7 Hz), 1.49 (6 H, d, *J* 7 Hz), 3.6 (2 H, m, *J* 7 Hz), 3.85 (2 H, s), 5.60 (2 H, m, aromatic), 6.8 (3 H, m, aromatic), 7.5 (4 H, m, aromatic), 8.25 (2 H, m, aromatic), and 8.6 (2 H, m, aromatic).

The slower reactions of the dienone with dimethyl fumarate and dimethyl maleate were each conducted with *ca.* 40 mg of the dienone and 200 mg of the dienophile in boiling toluene under nitrogen (3 h). Isolation by crystallisation of the evaporated products from methanol gave the respective adducts. The *dimethyl fumarate adduct* had m.p. 186—188° (Found: C, 76.0; H, 6.25. $C_{29}H_{30}O_5$ requires C, 76.0; H, 6.6%), δ 1.15—1.67 (12 H, 7 observed lines of 8 expected, 4 non-equivalent Me), 3.2 (3 H, s), 3.2 (1 H, d, *J* 5 Hz), 3.45 (2 H, m), 3.78 (3 H, s), 4.07 (1 H, d, *J* 5 Hz), 7.62 (4 H, m, aromatic), 8.3 (2 H, m, aromatic), and 8.72 (2 H, m, aromatic). The *dimethyl maleate adduct* had m.p. 222—224° (Found: C, 75.8; H, 6.25), δ 1.25 (6 H, d *J* 7 Hz), 1.4 (6 H, d, *J* 7 Hz), 3.2 (6 H, s, OMe), 3.5 (2 H, m), 3.9 (2 H, s), 7.56 (4 H, m, aromatic), 8.4 (2 H, m, aromatic), and 8.7 (2 H, m, aromatic).

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