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REACTION OF TETRAPHENYLCYCLOPENTADIENONE WITH CYCLIC OLEFINS: AN NMR PROBE OF ADDUCT STEREOCHEMISTRY

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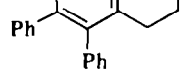
Abstract—The Diels Alder adducts of tetraphenylcyclopentadienone with cyclohexene and norbornene are reported. The effect of cyclic olefin adduct stereochemistry on the multiplicity pattern in the aromatic region of the proton spectrum is discussed as a probe to adduct stereochemistry with this diene system.

INTRODUCTION

Reaction of tetraphenylcyclopentadienone (tetracyclone) with cyclic olefins has been the subject of a vast literature.[1] The investigation, and elegance of such work has been hampered by difficulty in determining adduct stereochemistry. We now report the isolation and characterization of the *endo*- and *exo*-adducts of tetracyclone with cyclohexene, and coupled with other relevant studies, now suggest that the aromatic proton region of the NMR spectra of these adducts can, with caution, be useful in determination of adduct stereochemistry.

RESULTS AND DISCUSSION

Reaction of tetracyclone with cyclohexene was first examined[2] in 1939. The reaction was reported to occur only with great difficulty, requiring 10–12 hr heating in a sealed vessel at 280°. Under these conditions a solid, m.p. 163°, was isolated, and after extensive recrystallization, 1,2,3,4-tetraphenyltetralin (**1**), m.p. 271–3° was obtained.



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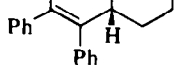

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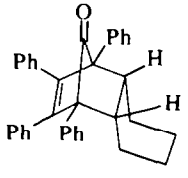

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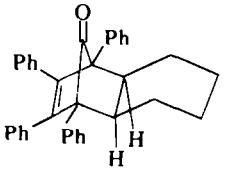

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During the course of other investigations we required an authentic sample of 1,2,3,4-tetraphenyl-4a,5,6,7,8,8a-hexahydronaphthalene (**2**) and to this end we reexamined the reaction of tetracyclone with cyclohexene. A solution of tetracyclone in cyclohexene was heated under reflux for 4 weeks after which time the reaction solution was still highly colored. Careful chromatography on silica gel facilitated the isolation of both the *endo*- and *exo*-adducts (**3** and **4**) with the only other product isolated being unchanged tetracyclone of intermediate polarity on silica gel between the less polar *endo*- adduct (**3**) and the more polar *exo*- adduct (**4**). The structure of the adducts follows from the preferential *endo*- mode of $[\pi^4s + \pi^2s]$ cycloaddition reactions and from the known magnitude of the solvent shift for *exo*- and *endo*- hydrogens of norbornan-7-ones.[3] For norbornan-7-ones the *endo*-hydrogens show a larger shift to higher field relative to *exo*-hydrogens in changing solvent from $CDCl_3$ to C_6H_6.[3] For adducts **3** and **4** the *exo*-hydrogens of the *endo*-adduct (**3**) shift 0.1 ppm upfield while the *endo*-hydrogens of the *exo*-adduct (**4**) show a 0.27 ppm upfield shift.

When the cycloaddition reaction of tetracyclone and cyclohexene was carried out at higher termperatures (100°) no *exo*-adduct (**4**) could be isolated. In addition to *endo*-adduct (**3**), 1,2,3,4-tetraphenyltetralin (**1**), 1,2,3,4-tetraphenyl-4a,5,6,7,8,8a-hexahydronaphthalene (**2**) and 2,3,4,5-tetraphenylcyclopent-2-en-1-one were isolated. Although the dihydrotetralin (**2**) could not be isolated free of tetraphenyltetralin (**1**), its presence in the mixture was established by oxidation with D.D.Q. to tetraphenyltetralin (**1**). Fortunately, examination of the NMR spectrum of the mixture of **1** and **2** enabled the proton signals for diene (**2**) to be assigned, in accord with the initial objectives of this study. The *endo*-adduct (**3**) underwent photodecarbonylation to dihydrotetralin (**2**), but irradiation of the *exo*-adduct (**4**) resulted in complex product formation.

Further examination of the NMR spectra of adducts **3** and **4** and a number of related adducts of tetracyclone with 3-, 4- and 5-membered ring cyclic olefins revealed an interesting pattern in the aromatic region of the spectra (Fig. 1). The parent ketone of this series, 1,2,3,4-tetraphenylnorbornen-7-one (**5**),[4] shows a well separated 10 proton multiplet and sharp spike for the phenyl protons at δ6.92 and 7.30, respectively. A similar aromatic pattern is observed for ketones **4** and **7**[5] while for adduct **11**[6] the same pattern is observed, but the peaks are reversed in order.

The upfield aromatic signsla (i.e. $<\delta$7.0) of **5**, as well as **4** and **7**, are assigned to the C2, C3-phenyl protons on the basis that phenyl crowding requires a mutual twisting, perhaps to different extents, of all phenyl rings with the result that the inner (C2, C3) phenyl protons are internally shielded by the neighboring twisted phenyls. A similar shielding effect is observed for the inner phenyl protons of tetralin (**1**), dihydrotetralin (**2**), 1,2,3,4-tetraphenylbenzene and 1,2,3,4-tetraphenyltropylium perchlorate.[7] A recent report by House *et al.*,[8] provides more convincing support for this assignment in that 1,8-diphenylanthracene (**6a**), like the monophenylanthracene

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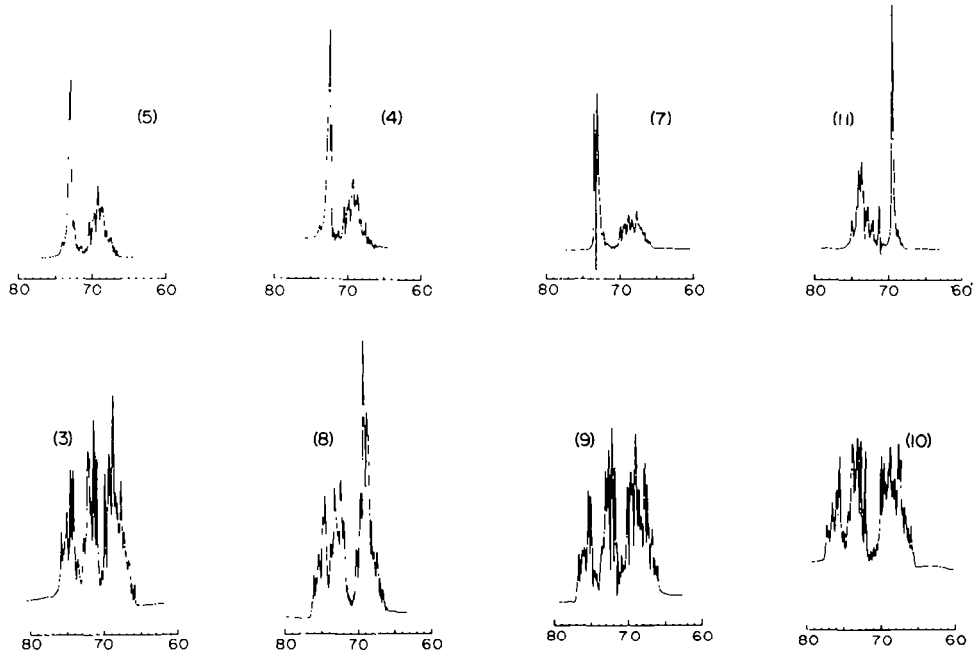
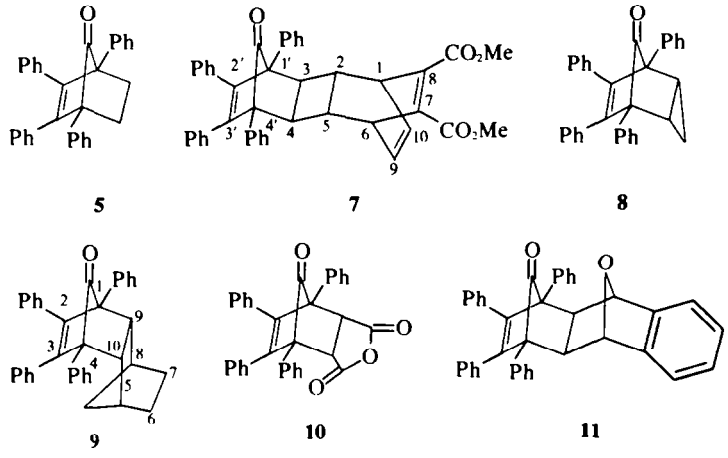
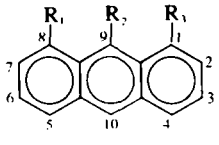


Fig. 1. Partial NMR spectra (aromatic region) for tetracyclone adducts 3, 4, 5, and 7–11 measured at 60 MHz in $CDCl_3$.



derivatives, shows no aromatic resonance at higher field than δ7.0 whereas in the 1,9-diphenyl compound (**6b**) the phenyl proton absorption lies above 7.0. Furthermore in the triphenyl derivative (**6c**) the resonance for all of the phenyl protons is shifted above δ7.0 with the central (C9) phenyl spike at highest fields.



6a: $R_1 = R_3 = Ph$; $R_2 = H$
b: $R_1 = R_2 = Ph$; $R_3 = H$
c: $R_1 = R_2 = R_3 = Ph$

Further analysis of the aromatic portion of the NMR spectrum of ketones **4**, **5** and **7** permits the following tentative conclusions to be drawn regarding the relative conformation of the 4 phenyl rings. The C2, C3-phenyl protons of ketone **5** occur as a broadened multiplet as opposed to a sharp singlet for the C1, C4-phenyls, suggesting that the C2, C3-phenyls lie substantially in the plane of the C2, C3-double bond. Such an arrangement would favor twisting of the C1, C4-phenyls as shown in

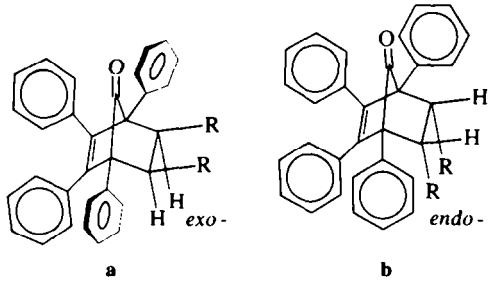


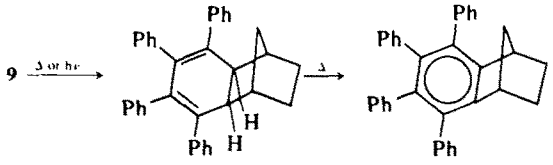
Fig. 2.

Fig. 2(a). A particularly notable consequence of this structure is the simplicity of the downfield C1, C4-phenyl absorptions in the NMR spectrum. The NMR spectra for *exo*-adducts **4** and **7**, where the *exo*-substituents should have no marked steric effect on the otherwise preferred geometry of the C1, C4-phenyls, exhibit a similar phenyl absorption pattern.

The simplicity of the downfield (C_1, C_4) phenyl proton resonance in the *exo*-adducts contrasts sharply with the observed aromatic pattern for tetracyclone adducts **3**, **8**, **9**

and **10**. Thus each of the latter adducts displays a series of three complex multiplets in the range δ6.5–7.7 with the upfield multiplet again being assigned to the 10 protons of the C2, C3-phenyl substituents. The remaining multiplets are assigned to the 4 ortho and 6 meta, para protons of the C1, C4-phenyl rings. The more complex aromatic pattern observed for these four adducts may be rationalized again on a conformational basis, assuming, for the moment, they have the opposite (namely *endo*) stereochemistry to the *exo*-adducts previously discussed. It is reasoned that *endo*-substituents should disrupt the preferred geometry of the bridge C1, C4-phenyl groups forcing them into a more nearly orthogonal relationship with the bridge carbonyl plane (Fig. 2b). This change should markedly affect the diamagnetic shielding of the C1, C4-phenyl protons thus accounting in part for the increased multiplicity observed in the aromatic proton spectra.†

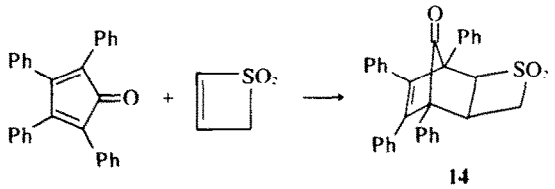
The *endo* stereochemistry for cyclopropene adduct (**8**)[7] has been previously established on the basis of reactivity comparisons and cyclopropyl proton chemical shift and coupling parameters.[9] The *endo*-assignment for cyclohexene adduct **3** is supported by the solvent shift data previously described. The *exo*, *endo* stereochemistry of the previously unreported norbornene-tetracyclone adduct (**9**) is supported by the lack of coupling of vicinal bridgehead protons H9, H10 (δ6.88, Wh/2 = 2.5 Hz) with the adjacent bridgehead protons H5, H8. Furthermore, the enhanced chelotropic reactivity of ketone **9** is consistent with that found for similar *exo*, *endo* fused norbornen-7-ones,[10,11] but inconsistent with that expected of the more stable *exo*, *exo* fused ketones.[12] Thus, extensive decarbonylation of ketone **9** occurred on simple refluxing in chloroform solution to afford a mixture of 1,3-diene **12** and the aromatized hydrocarbon **13**. The structure of **12** was established by oxidation to **13** with DDQ. Photodecarbonylation of ketone **9** also afforded diene **12**.



12 **13**

To our knowledge the stereochemistry of the maleic anhydride-tetracyclone adduct (**10**) has never been established despite the fact this adduct has been known for almost 40 years.[1] The multiplicity pattern (Fig. 1) in the aromatic region of the NMR spectrum of **10** clearly indicates *endo*-stereochemistry; however, care must be exercised in interpreting such data since adduct **11**, apparently having *exo*-stereochemistry, exhibited the upfield C2, C3- phenyl protons as a singlet (Fig. 1). This is the only example of this anomaly noted in our laboratories. With due regard for this cautionary note, the aromatic proton multiplicity pattern for tetracyclone adducts should, at the least, provide a useful empirical assist to the assignment of stereochemistry in this series.

The usefulness of the method may be further illustrated by a final example from the recent literature.[13] In this work the interesting thermal transformations of the tetracyclone-thiete sulfone adduct(s) were described;[13]



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however, the stereochemistry of the isolated crystalline adduct **14** was not assigned. On the basis of the reported[13] NMR multiplicity pattern for the phenyl protons [(60 MHz; $CDCl_3$) δ7.3 (10H, s), 6.58–7.1 (10H, complex mult.)] we tentatively assign the *exo* stereochemistry to **14**. In view of the rather low yield (7.8%) for isolation of **14** one cannot rule out formation of the corresponding *endo* adduct, although preferential *exo* adduction is to be expected for reaction of arylcyclopentadienones with cyclobutene dienophiles.[14]

EXPERIMENTAL

M.ps were determined on a Hoover–Thomas apparatus and are uncorrected. IR spectra were recorded as mulls (Nujol), films, or solids (KBr) on a Perkin–Elmer 137 spectrophotometer. UV spectra were recorded on a Cary 15 spectrophotometer. NMR spectra were recorded on a Varian A-60A (60 MHz) spectrometer in $CDCl_3$ solns, unless otherwise stated, using $CHCl_3$ and TMS as internal standards. Coupling constants and chemical shifts were derived by first order analysis and the latter are reported in order of decreasing δ, with multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Mass spectra were determined on a Hitachi RMU-6E spectrometer operating at 70 eV. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia.

Reaction of tetraphenylcyclopentadienone with cyclohexene

(a) A soln of tetraphenylcyclopentadienone (500 mg) in cyclohexene (200 ml) was heated under reflux for 4 weeks. The volume was reduced *in vacuo* at room temp. and the product adsorbed onto silica (50 g). Elution with petroleum ether (20–40°) afforded the *endo*-adduct **3** (120 mg), recrystallized from petroleum ether (30–60°), m.p. 180–181° (vigorous evolution of CO on melting) (Found: C, 89.9; H, 6.5. $C_{35}H_{30}O$ requires: C, 90.1; H, 6.5%); $\lambda_{max}^{CH_2Cl_2}$ (ε) 220 (61,400), 260 (sh) nm (16,960); δ 7.42 (4H, m, $W_{\frac{1}{2}}$ = 15 Hz) and 7.08 (6H, m, $W_{\frac{1}{2}}$ = 12 Hz) (C1, C4–Ph), 6.87 (10H, m, $W_{\frac{1}{2}}$ = 17 Hz; C2, C3–Ph), 2.75 (2H, bm; *expo*-methine H), 0.6–1.9 (8H, bm; methylene H). $\delta^{C_6D_6}$ 2.65 (2H, bm; *exo*-methine H). Mass spectrum: *m/e* (70 eV) 466 (M^+, 12%), 438 (M^+–CO, base peak).

Further elution with petroleum ether afforded tetraphenylcyclopentadienone (300 mg) and *exo*-adduct **4** (80 mg), m.p. 238–239° (vigorous gas evolution on melting-turns red) (Found: C, 88.2; H, 5.9‡ $C_{35}H_{30}O$ requires: C, 90.1; H, 6.5%); $\lambda_{max}^{CH_2Cl_2}$ (ε) 220 (48,000), 270 nm (17,340); δ 7.38 (10H, s; C1, C4–Ph), 6.93 (10H, m, $W_{\frac{1}{2}}$ = 15 Hz; C2, C3–Ph), 3.02 (2H, bs; *endo*-methine H), 1.3–2.2 (8H, bm; methylene H). $\delta^{C_6D_6}$ 2.75 (2H, bs; *endo*-methine H). Mass spectrum: *m/e* (70 eV) 466 (M^+, 2%), 438 (M^+–CO, base peak).

(b) A solution of tetraphenylcyclopentadienone (1 g) in cyclohexene (10 ml) was heated in a sealed tube at 100° for 4 weeks. Chromatography on silica gel (100 g) gave an amorphous white

†The NMR assignments for the C1, C4- and C2, C3-phenyl protons has been confirmed in more recent work by NMR examination of the ethylene and selected cyclic olefin adducts (*exo* and *endo*) of 3,4-(bis-*p*-substituted phenyl)-2,5-diphenylcyclopentadienones. In each of the adducts examined the AA'BB' pattern for the substituted phenyl protons appeared as the highest field aromatic signal in full accord with the above assignment of the upfield aromatic signal to the C2, C3 phenyl protons. This confirmation of aromatic proton assignments was extended to the isobenzofuran adduct (**11**).

‡Ketone **4** consistently gave low carbon-hydrogen microanalyses despite repeated recrystallization. We attribute this problem to the sensitivity of **4** to photochemical decarbonylation and subsequent oxygenation of resultant product(s) (*vide infra*).

solid (450 mg), m.p. 193–194° [ν_{max} 1570 and 1590 cm^{-1}; mass spectrum: *m/e* (70 eV) 438 (M^+), 436 (M^+)], consisting of a mixture (55:45) of **2** [δ 7.06 (10H, s; Cl, C4–Ph), 6.73 (10H, s; C2, C3–Ph), 3.05 (2H, irr t; J = 4, 3 Hz; H9, 10)] and **1**. Further elution with petroleum ether gave 300 mg of *endo*-adduct **3**, m.p. 180–181°. Continued elution with petroleum gave tetracyclone (50 mg) followed by 2,3,4,5-tetraphenylcyclopent-2-en-1-one (190 mg), m.p. 170–171°; ν_{max} 1680 cm^{-1}; δ 7.0–7.35 (20 H, aromatic multiplet), 4.55 (d, $J_{2,3}$ = 2.5 Hz; H3), 3.42 (d, $J_{2,3}$ = 2.5 Hz; H2; *lit. cit.*[15] J_{AB} = 2.5 Hz).

Oxidation of 1,2,3,4-*tetraphenyl*-4a,5,6,7,8,8a-*hexahydronaphthalene* (**2**)

To a soln of a mixture (100 mg from the above reaction) of **2** and **1** DDQ (100 mg) was added and the resulting mixture allowed to stand overnight at room temp. The mixture was filtered through a silica gel column (100 g) and collection of the colorless fraction gave, after solvent evaporation and recrystallization, **1**, m.p. 273–274° (*lit. cit.*[2] 271–3°); δ 7.10 (10H, s; Cl, C4–Ph), 6.75 (10H, s; C2, C3–Ph) 2.53 (4H, m; H5, 8), 1.70 (4H, m; H6, 7).

Photolysis of endo-*adduct* (**3**) *and* exo-*adduct* (**4**)

A soln of *endo*-adduct **3** (30 mg) in deoxygenated cyclohexane (30 ml) was photolyzed (2534 Å) in an atmosphere of N_2 for 2 hr. After removal of solvent an NMR spectrum exhibited peaks in the aromatic region (δ 6.74 and 7.06) consistent with the formation in significant yield of **2**. The mixture was homogeneous to TLC, but the complex nature of the NMR spectrum suggested the presence of other products.

A solution of the *exo*-adduct **4** (20 mg) was photolyzed as above, to give a crude product mixture which, according to NMR analysis, contained no significant quantity of **2**.

Reaction of tetraphenylcyclopentadienone with norbornene

A soln of tetraphenylcyclopentadienone (1 g) and norbornene (3 g) in chloroform (20 ml) was heated under reflux for 2 weeks. The volume was reduced *in vacuo* at room temp. Adsorption onto silica gel (100 g) and elution with petroleum ether (30–60°) gave norbornene followed by an amorphous material (390 mg) which on recrystallization from MeOH had m.p. 195–215°; ν_{max} 1590, 1570 cm^{-1}. This material consisted of a (40:60) mixture of diene **12** [δ 7.07 (10H, s; Cl, C4–Ph), 6.75 (10H, s; C2, C3–Ph), 3.12 (2H, unsym. d; allylic bridgehead H)] and aromatic compound **13** [δ 7.14 (10H, s; C1, C4–Ph), 7.00 (10H, s; C2, C3–Ph), 3.37 (2H, m; bridgehead H)].

Further elution with petroleum ether gave after recrystallization from petroleum ether the *endo*-adduct **9** (380 mg), m.p. 211–212° (turns pink and evolves CO on melting). (Found: C, 90.2; H, 6.4. $C_{36}H_{30}O$ requires: C, 90.3; H, 6.3%); ν_{max}^{CO} 1670 cm^{-1}; $\lambda^{CH_2Cl_2}$ (ϵ) 220 (34,200), 260 (sh) nm (9,900); δ 7.55 (4H, m, $W_{\frac{1}{2}}^h$ = 10 Hz) and 7.30 (6H, m, $W_{\frac{1}{2}}^h$ = 12 Hz) C1, C4–Ph), 6.90 (10H, m, $W_{\frac{1}{2}}^h$ = 20 Hz; C2, C3–Ph), 2.75 (2H, unsym. d, J = 1.5 Hz; H9, 10), 2.52 (2H, m; bridgehead H5, 8), 0.6–1.9 (6H, bm; methylene H). Mass spectrum: *m/e* (70 eV) 478 (M^+, <1%), 450 ($M^+ - CO$, base peak).

Photolysis of endo-*adduct* (**9**)

A soln of *endo*-adduct **9** (70 mg) in deoxygenated cyclohexane (60 ml) was irradiated (2537 Å) in a N_2 atmosphere for 90 min. After removal of solvent the NMR spectrum indicated significant formation of diene **12**.

Oxidation of diene (**12**)

To a soln of the 40:60 mixture (100 mg) of diene **12** and aromatic compound **13** from reaction of norbornene with tetracyclone, in benzene, was added DDQ and the resulting mixture allowed to stand at room temp. overnight. The mixture was filtered through silica gel (100 g), and the colorless fraction collected and evaporated to give an amorphous solid, shown by NMR to be a (20:80) mixture of diene **12** (δ 7.07, 6.75 and 3.12) and aromatic compound **13** (δ 7.14, 7.00 and 3.37).

1,2,3,4-*Tetraphenyl norbornen-7-one* (**5**).[4] M.p. 202–203° (dec), δ 7.30 (10H, s; C1, C4–Ph), 6.92 (10H, m; C2, C3–Ph), 2.2–3.0 (4H, AA'BB'; methylene H).

Adduct of tetracyclone with:

(a) *cyclopropene*.[7] m.p. 168° (dec), δ 7.48 (4H, m, $W_{\frac{1}{2}}^h$ = 10 Hz) and 7.30 (6H, m, $W_{\frac{1}{2}}^h$ = 12 Hz) (Cl, C4–Ph), 6.87 (10H, m, $W_{\frac{1}{2}}^h$ = 10 Hz; C2, C3–Ph), 2.17 (2H, dd, $J_{2,3x}$ = *ca.* 7 Hz, $J_{2,3n}$ = *ca.* 3.5 Hz; H2,4), 1.37 (dt, $J_{3n,3x}$ = *ca.* 6.5 Hz, $J_{2,3x} = J_{4,3x}$ = *ca.* 7 Hz; H3x), 0.82 (dt, $J_{3n,3x}$ = *ca.* 6.5 Hz, $J_{2,3n} = J_{4,3n}$ = *ca.* 3.5 Hz, H3n).

(b) *Oxabenznorbornadiene*.[6] m.p. 180–182° (dec), δ 7.38 (14H, m, $W_{\frac{1}{2}}^h$ = 20 Hz; benzo AA'BB' and C1, C4–Ph) 6.95 (10H, s; C2, C3–Ph), 5,80 (2H, s; benzylic bridgehead H), 3.07 (2H, s; *endo*-bridgehead H).

(c) *maleic anhydride*.[1] m.p. 220–222° (dec), δ 7.64 (4H, m, $W_{\frac{1}{2}}^h$ = 10 Hz) and 7.35 (6H, m, $W_{\frac{1}{2}}^h$ = 13 Hz) (C1, C4–Ph), 6.9 (10H, m, $W_{\frac{1}{2}}^h$ = 16 Hz; C2, C3–Ph), 4.47 (2H, s; H5x, 6x).

(d) *Dimethyl* 7,8-*tricyclo*[4.2.2.0^{2,5}]*deca*-3,7,9-*triene dicarboxylate*.[5] m.p. 176–179° (dec), δ 7.35 (2H, s; vinyl), 7.30 (10H, s; C1', C4'–Ph), 6.84 (10H, m, $W_{\frac{1}{2}}^h$ = 17 Hz; C2', C3'–Ph), 4.30 (2H, bm; H1,6), 3.50 (6H, s; ester CH_3), 2.65 (2H, m; H2,5), 2.13 (2H, m; H3,4).

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