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SYNTHESIS OF 1,2-ACENAPHTHO-3,8-DISUBSTITUTED-DERIVATIVES OF CYCLO-OCTATETRAENE

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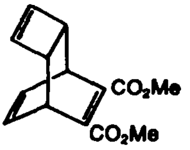
Abstract—Acecyclone and related cyclopentadienones 11 react with dimethyl tricyclo[4.2.0.0^{2,5}]deca-3,7,9-triene-7,8-dicarboxylate 1 in refluxing xylene to afford the cyclo-octatetraenes 12, via a sequence involving [4+2]π-cycloaddition, cheletropic loss of carbon monoxide, extrusion of dimethyl phthalate by [4+2]π-cycloreversion, and finally valence isomerisation by *retro*-6π electrocyclisation. NMR evidence indicates that the products 12 contain rigid, bond-fixed, non-planar cyclo-octatetraene rings.

Cycloaddition to the 3,4-olefinic bond of the cyclo-octatetraene-dimethyl acetylenedicarboxylate adduct 1, and subsequent extrusion of dimethyl phthalate by thermal [4+2]π-cycloreversion (Alder–Rickert reaction[1]), leads to 3,4-annulated cyclobutenes (see Ref. 2). This procedure can be adapted[3] to produce 2,3,4,5-tetrasubstituted bicyclo[4.2.0]octa-2,4,7-trienes 2, valence isomers of 1,2,3,8-tetrasubstituted cyclo-octatetraenes 3; the latter are of current interest[4-6] because of their resistance (in various degrees) to ring-inversion and bond-shift processes,† the attainment of planarity by the C_8-ring being inhibited by contiguous substituent interactions. Thus reaction of hemicyclone (2,5-dimethyl-3,4-diphenylcyclopentadienone) to 1 gives a 1:9 mixture of *endo* and *exo* adducts, 5 and 6 respectively, and thermolysis of pure 6 at 190° then affords the carbonyl-bridged compound 7.[3] Thermal decarbonylation of such systems, which should result in products of structure 2, is sometimes troublesome and McCay and Warrener[7] resorted to photochemical extrusion of the carbonyl bridge (see Ref. 8) in the preparation of 8, which at 65° was transformed into the cyclo-octatetraene 9 (in equilibrium with the valence tautomer 10).

We have now found that acecyclone and its analogues 11 react with 1 in refluxing xylene to give the cyclo-octatetraenes 12 directly. Some of the cycloadditions were carried out in refluxing toluene, when the isolated products proved to have structure 13. Thus cheletropic loss of carbon monoxide from the initial [4+2]cycloadducts 14 (stereochemistry uncertain) occurred under conditions which were less vigorous than those required for the Alder–Rickert extrusion of dimethyl phthalate [the ready thermal decarbonylation of certain acecyclone adducts has been noted previously;[9] the adduct of 1-methylcyclopropene loses carbon monoxide even below 10°[9b]]. Compounds 13a, 13b, 13f and 13g were prepared in this way, and were shown to afford the cyclo-octatetraenes 12a, 12b, 12f and 12g respectively in boiling xylene. The reaction sequence leading to the final products 12 may therefore be formulated as shown in Scheme 1.

The ^{1}H NMR spectra of the symmetrically substituted cyclo-octatetraenes 12a, 12c, 12e and 12g indicated the presence of two pairs of vinylic protons with a small mutual coupling in accord with the basic structure 12 (see, e.g. benzocyclo-octatetraene[10]); the evidence excludes the bond-shift isomers 15, which would in any case be highly strained. The two sets of methyl protons in the



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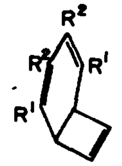

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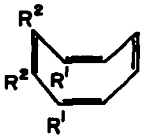
8: $R^1 = Me$, $R^2 = Ph$



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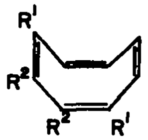

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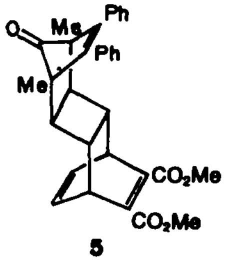

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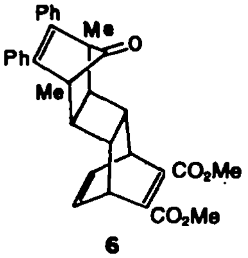

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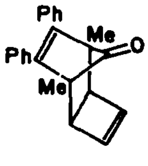

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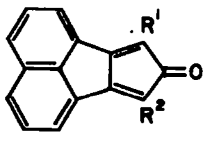
†Bond-shift leads to the 1,2,3,4-tetrasubstituted isomers 4.



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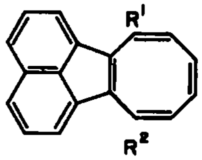
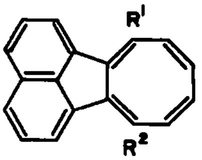


12

a: R^1 = R^2 = Ph
b: R^1 = Ph, R^2 = Me
c: R^1 = R^2 = Me
d: R^1 = Me, R^2 = Pr^i
e: R^1 = R^2 = Pr^i
f: R^1 = Et, R^2 = CO$_2$Et
g: R^1 = R^2 = CO$_2$Et



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isopropyl group of **12d** gave 3H doublets at different chemical shifts, and they must therefore be diastereotopic. This is consistent with the presence of a "rigid" tub-shaped cyclo-octatetraene ring, since rapid ring-inversion would render these Me protons isochronous.[11] Similar effects were observed for the Me protons in **12e**, and for the methylene protons of the ester groups in **12g**.† No coalescence of the two Me proton signals shown by **12e** could be achieved even at 200° (soln in hexachlorobutadiene).

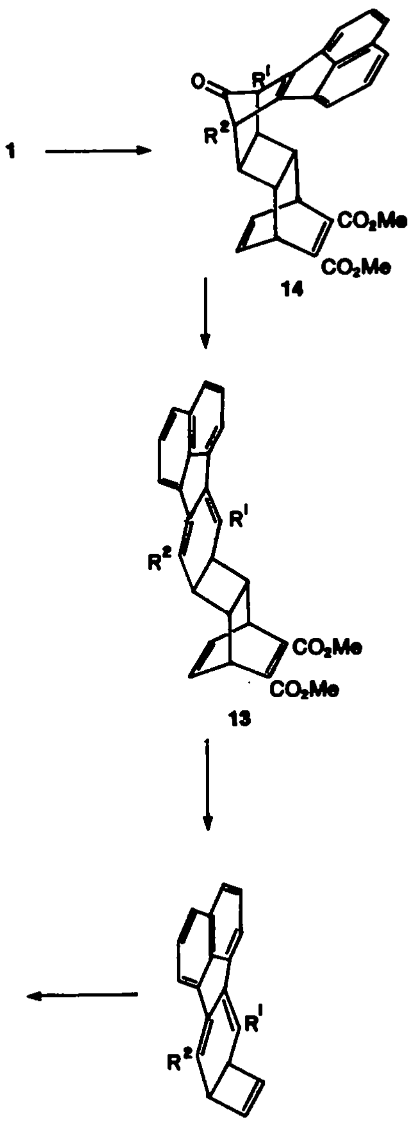
EXPERIMENTAL

Unless stated otherwise, NMR spectra were measured at 100 MHz for solns in CDCl$_3$: IR spectra were determined for Nujol mulls.

Compound **1** was obtained as described by Anderson and Fagerburg.[12] The following cyclopentadienones were prepared according to the superscribed refs: **11a**,[13] **11b** (as the dissociating dimer),[14] **11c** (as the dissociating dimer),[14]‡ **11e**,[14] **11g**.[14]

The methyl-isopropyl compound **11d** (as the dissociating dimer). KOH (1.0 g) in MeOH (10 ml) was added to acenaphthoquinone (3.8 g) and 5-methylhexan-3-one (5 ml) in the same solvent (30 ml), and the mixture was stirred and heated under reflux for 3 hr. Most of the MeOH was removed under reduced pressure, water (100 ml) was added, and the mixture was extracted with benzene (500 ml). The benzene layer was washed with water, dried (MgSO$_4$), and finally evaporated to yield **11d** as its Diels–Alder dimer; yellow crystals (4.26 g, 79%), m.p. 148–149° (from MeOH) (Found: C, 87.3; H, 6.15. C$_{38}$H$_{32}$O$_2$ requires: C, 87.7; H, 6.2%); IR ν_{max} 1700, 1695, 1645 cm^{-1}. The NMR spectrum revealed a mixture of monomer and dimer in soln (CCl$_4$).

The ethyl-ethoxycarbonyl compound **11f**. To acenaphthoquinone (1.9 g) and ethyl 3-oxohexanoate (3.5 ml) in EtOH (15 ml) was added KOH (0.5 g) in the same solvent (5 ml), and the mixture was stirred at 45° for 3 hr. The EtOH was removed under reduced pressure, and the products were partitioned between water (100 ml) and toluene (500 ml); the organic layer was discarded. The aqueous layer was then extracted thoroughly with toluene (2 × 500 ml). Removal of the solvent gave **11f** (1.07 g, 21%) as deep purple crystals, m.p. 135–136° (from CCl$_4$) (Found: C, 79.3; H, 5.4. C$_{20}$H$_{16}$O$_3$ requires: C, 78.9; H, 5.3%); IR ν_{max} 1730, 1685 cm^{-1}; NMR τ 1.45 (1 H, d, J 7 Hz), 2.0–2.5 (5 H), 5.59 (2 H, q, J 7 Hz), 7.44 (2 H, q, J 7 Hz), 8.53 (3 H, t, J 7 Hz), 8.76 (3 H, t, J 7 Hz).



Scheme 1.

The decarbonylated Diels–Alder adducts **13**. A mixture of **11** (or its dissociating dimer; 1.0 g) and adduct **1** (2.5 g) in toluene (20 ml) was heated under reflux for 15 hr. Removal of the solvent under reduced pressure, and treatment of the residue with ether, then afforded **13**, which was recrystallised from ether–acetone.

Compound **13a**, yield 31%, m.p. 201–202° dec. (Found: C, 83.8; H, 5.5. C$_{40}$H$_{30}$O$_4$ requires: C, 83.6; H, 5.3%); IR ν_{max} 1735, 1715, 1635, 1600 cm^{-1}; NMR τ 2.45–2.55 (12 H), 2.79 (2 H, d, J 7 Hz), 3.37 (2 H, d, J 8 Hz), 3.47 (2 H, dd, J 3.5 and 3 Hz), 6.0–6.1 (2 H), 6.26 (6 H, s), 7.15–7.25 (2 H), 7.25–7.35 (2 H).

Compound **13b**, yield 35%, m.p. 189–191° dec. (Found: C, 82.0; H, 5.5. C$_{35}$H$_{28}$O$_4$ requires: C, 82.0; H, 5.5%); IR ν_{max} 1735 sh, 1715, 1620, 1595 cm^{-1}; NMR τ 2.35–2.7 (9 H), 2.89 (1 H, d, J 8 Hz), 3.3–3.6 (3 H), 5.65–5.8 (1 H), 6.0–6.15 (1 H), 6.23 (3 H, s), 6.27 (3 H, s), 7.3–7.65 (4 H), 7.74 (3 H, s).

Compound **13f**, yield 65%, m.p. 168–170° dec. (Found: C, 76.0; H, 5.9. C$_{33}$H$_{30}$O$_6$ requires: C, 75.8; H, 5.8%); IR ν_{max} 1735, 1715, 1700, 1650, 1635, 1600 cm^{-1}; NMR τ 1.34 (1 H, d, J 7 Hz), 2.25–2.6 (5 H), 3.43 (2 H, dd, J 3.5 and 3 Hz), 5.55–5.85 (4 H), 6.27 (6 H, s), 7.1–7.65 (6 H), 8.54 (3 H, t, J 7 Hz), 8.75 (3 H, t, J 8 Hz).

Compound **13g**, yield 70%, m.p. 169–170°. (Found: C, 71.8; H,

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†The effect was not clearly observable in the spectrum of **12f**.
‡Could not be obtained pure.

5.3. $C_{34}H_{30}O_8$ requires C, 72.1; H, 5.3%); IR ν_{max} 1745, 1710, 1635, 1600 cm^{-1}; NMR τ 1.53 (2 H, d, *J* 7 Hz), 2.20 (2 H, d, *J* 8 Hz), 2.43 (2 H, dd, *J* 8 and 7 Hz), 3.44 (2 H, dd, *J* 4 and 3 Hz), 5.57 (4 H, q, *J* 8 Hz), 5.65–5.8 (2 H), 6.25 (6 H, s), 7.2–7.3 (2 H), 7.4–7.55 (2 H), 8.52 (6 H, t, *J* 8 Hz).

The cyclo-octatetraenes 12

(i) *From the decarbonylated adducts* 13. The decarbonylated adduct 13 (1.0 g) was heated in refluxing xylene† (15 ml) for 4 hr. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica. Elution with hexane-toluene then gave 12, which was recrystallised from MeOH.

(ii) *From the cyclopentadienones* 11 *directly*. A mixture of 11 (or its dissociating dimer; 1.0 g) and the adduct 1 (2.5 g) in xylene (15 ml) was heated under reflux for 15 hr. After removal of the xylene under reduced pressure, the residual cyclo-octatetraene was purified as described above.

Compound 12a, red crystals [37%, Method (i); 63%, Method (ii)], m.p. 181–182° (Found: C, 94.65; H, 5.3. $C_{30}H_{20}$ requires: C, 94.7; H, 5.3%); NMR τ 2.34 (2 H, d, *J* 8 Hz), 2.45–2.8 (12 H), 3.10 (2 H, d, *J* 7 Hz), 3.35–3.45 (2 Hz), 3.95–4.05 (2 H).

Compound 12b, orange crystals [53%, Method (i); 35%, Method (ii)], m.p. 103–105° (Found: C, 94.06; H, 5.9. $C_{25}H_{18}$ requires: C, 94.3; H, 5.7%); NMR τ 2.25–2.85 (10 H), 3.21 (1 H, d, *J* 7 Hz), 3.45–3.55 (1 H), 3.95–4.05 (1 H), 4.1–4.2 (2 H), 7.70 (3 H, d, *J* 1 Hz).

Compound 12c, orange crystals [7% (from the very crude cyclopentadienone), Method (i)], m.p. 135–136° (Found: C, 93.4; H, 6.5. $C_{20}H_{16}$ requires: C, 93.7; H, 6.3%); NMR τ 2.2–2.6 (6 H), 3.95–4.05 (2 H), 4.2–4.3 (2 H), 7.74 (6 H, d, *J* 1 Hz).

Compound 12d, orange gum [71%, Method (ii)], b.p. *ca.* 186°/0.4 mm. (Found: C, 93.1; H, 7.1. $C_{22}H_{20}$ requires: C, 92.9; H, 7.1%); NMR τ 2.3–2.7 (6 H), 4.1–4.15 (2 H), 4.2–4.35 (2 H), 7.0–7.3 (1 H), 7.80 (3 H, d, *J* 1.5 Hz), 8.70 (3 H, d, *J* 7 Hz), 8.98 (3 H, d, *J* 7 Hz).

Compound 12e, orange-yellow crystals [77%, Method (ii)], m.p. 112–113° (Found C, 92.3; H, 7.9. $C_{24}H_{24}$ requires: C, 92.3; H, 7.7%); NMR τ 2.15–2.55 (6 H), 3.95–4.05 (2 H), 4.1–4.2 (2 H), 7.03 (2 H, septet, *J* 7 Hz), 8.62 (6 H, d, *J* 7 Hz), 8.88 (6 H, d, *J* 7 Hz).

Compound 12f, orange-yellow gum [82%, Method (i)], b.p. *ca.* 216°/0.7 mm. (Found: C, 83.7; H, 5.3. $C_{23}H_{20}O_2$ requires: C, 84.1; H, 5.2%); NMR τ 2.3–2.8 (7 H), 4.15–4.25 (3 H), 5.83 (2 H, q, *J* 7 Hz), 7.46 (2 H, q, *J* 7 Hz), 8.83 (3 H, t, *J* 7 Hz), 8.95 (3 H, t, *J* 7 Hz).

Compound 12g, yellow crystals [72%, Method (i)], m.p. 119–120° (Found: C, 77.3; H, 5.4. $C_{24}H_{20}O_4$ requires: C, 77.4; H 5.4%); NMR τ 2.28 (2 H, dd, *J* 7 and 2 Hz), 2.55 (2 H, d, *J* 8 Hz), 2.6–2.7 (4 H), 4.0–4.05 (2 H), 5.6–5.95 (4 H), 8.81 (6 H, t, *J* 7 Hz).

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†Mesitylene was used for 13g.