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7b-Methyl-7bH-cyclopent[cd]indene, an Unsubstituted Tricyclic Aromatic [10]Annulene

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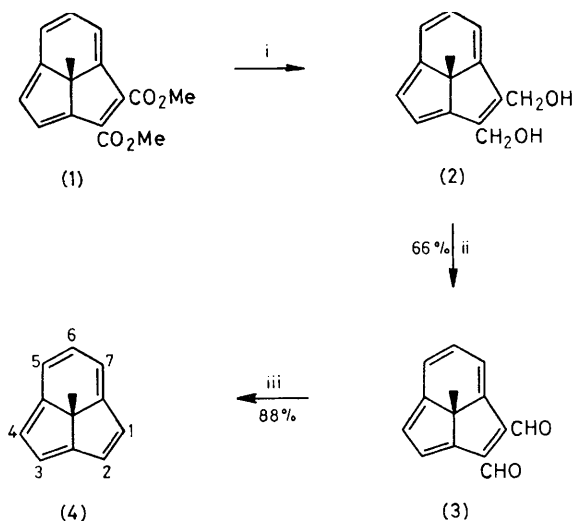
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Summary The aromatic tricyclic [10]annulene (**4**) has been synthesised by bis-decarbonylation of the dialdehyde (**3**); on heating (**4**) rearranged into the 2aH-isomer (**6**).

WE have recently described the synthesis of the first tricyclic [10]annulene derivative (**1**).¹ We now report the conversion of (**1**) into the parent [10]annulene (**4**) (Scheme) and some preliminary results on the chemistry of this new 10 π -electron aromatic system with an unsubstituted periphery.

The diester (**1**) was reduced with lithium aluminium hydride to the diol (**2**), which was immediately oxidised to the orange-red dialdehyde (**3**), † m.p. 76–77 °C, with barium manganate, a reagent which is particularly effective for the oxidation of benzylic alcohols.² The dialdehyde (**3**) was efficiently bis-decarbonylated using tris(triphenylphosphine)rhodium(i) chloride (2 equiv.) in refluxing benzene. Use of one equivalent of the 'catalyst' gave an inseparable mixture of the monoaldehydes. Attempts to prepare (**4**) by hydrolysis and bis-decarboxylation of (**1**) were unsuccessful.

The unsubstituted [10]annulene (**4**) is a volatile yellow oil which solidifies on cooling in ice, λ_{\max} (EtOH) 249sh (log ϵ 3.74), 282 (4.54), 335sh (3.52), 398sh (2.11), 439sh (2.57), and 450 nm (2.64). The ¹H n.m.r. spectrum (CDCl₃), which is consistent with a symmetrical structure and the existence of a diamagnetic ring current, shows a signal upfield of tetramethylsilane (at δ - 1.67) for the central methyl group. The peripheral hydrogen atoms are at δ 7.53–7.83



SCHEME. Reagents: i, LiAlH₄, Et₂O, 25 °C; ii, BaMnO₄, CH₂Cl₂, 40 °C; iii, RhCl(PPh₃)₃ (2 equiv.), C₆H₆, 80 °C. Overall yields of steps ii and iii are given.

(AB₂ system, 5-, 6-, and 7-H) and 7.89–7.92 (AB system, 1-, 2-, 3-, and 4-H) ($J_{5,6}$ 7 and $J_{1,2}$ 3 Hz).

Catalytic hydrogenation of the annulene (**4**) over 5% palladium-on-charcoal at room temperature and atmospheric

† Satisfactory spectral data were obtained for all new compounds.

pressure resulted in rapid uptake of hydrogen (5 mol) to give the fully saturated hydrocarbon (5).

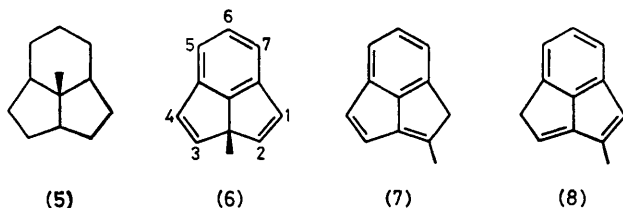
On heating in boiling xylene, (4) rearranged in a first-order reaction ($t_{1/2}$ 12 h) to 2a-methyl-2aH-cyclopent[cd]indene (6) by a [1,5]Me sigmatropic shift. The diester (1) rearranged similarly in xylene, with $t_{1/2}$ 3.5 h. However, the rearrangement of (4) was achieved in best yield (80%) by flash-vacuum pyrolysis at 400 °C/0.3 mmHg. The 2aH-isomer (6) is an oil, λ_{\max} (EtOH) 258 (log ϵ 4.04), 318sh (2.50), and 331sh nm (2.41). The ^1H n.m.r. spectrum confirms the symmetrical nature of the 2aH-isomer and shows δ (CDCl_3) 1.48 (2a-Me), 6.59 (2- and 3-H), 6.71 (1- and 4-H), 6.99 (5- and 7-H), and 7.15 (6-H) ($J_{1,2}$ 5 and $J_{5,6}$ 7 Hz).

Flash-vacuum pyrolysis of (4) at higher temperatures (600 °C) resulted in further rearrangement to give a 2:1

mixture of the more stable 1H-isomers (7) and (8) by [1,5]-methyl and -hydrogen shifts. The unsubstituted 1H-isomer, 1H-cyclopent[cd]indene has previously been prepared,^{4,5} and its reported u.v. spectrum is similar to that obtained from the mixture of (7) and (8).

The annulene (4) is sufficiently aromatic to be inert towards the powerful dienophile, 4-phenyltriazoline-3,5-dione (PTAD), in 1,2-dimethoxyethane at room temperature. However, at 80 °C a cycloadduct of (4) with two moles of PTAD is formed; no 1:1 adduct is observed, even with excess of (4), showing (4) to be less reactive than the olefinic 1:1 adduct.

The tricyclic [10]annulene (4) therefore has similar properties to Boekelheide's tetracyclic [14]annulene,⁶ in that it is readily hydrogenated, fails to form a complex with picric acid, and rearranges on heating by migration of the central methyl group to the periphery. Unlike Boekelheide's annulene, compound (4) appears to be photostable. The more detailed chemistry of this new aromatic system is under investigation.



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