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

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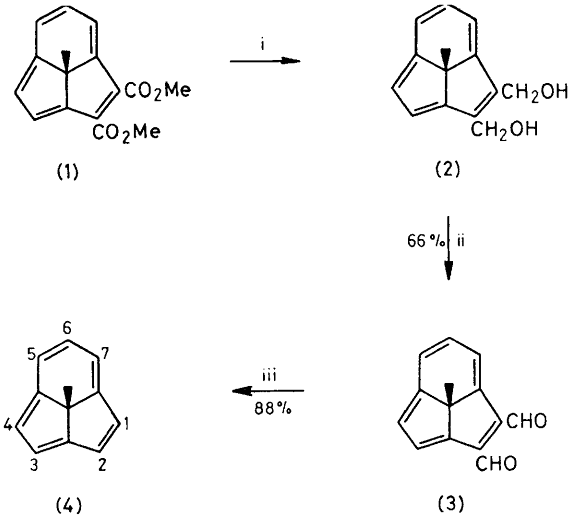
Summary The aromatic tricyclic [10]annulene (**4**) has been synthesised by bis-decarbonylation of the dialdehyde (**3**); on heating (**4**) rearranged into the 2a*H*-isomer (**6**).

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 10π-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 benzenes. 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, $\lambda_{\max}$ (EtOH) 249sh (log ϵ 3·74), 282 (4·54), 335sh (3·52), 398sh (2·11), 439sh (2·57), and 450 nm (2·64). The ^{1}H n.m.r. spectrum ($CDCl_3$), 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 (AB_2 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).



Scheme. *Reagents:* i, $LiAlH_4$, Et_2O, 25 °C; ii, $BaMnO_4$, CH_2Cl_2, 40 °C; iii, $RhCl(PPh_3)_3$ (2 equiv.), C_6H_6, 80 °C. Overall yields of steps ii and iii are given.

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

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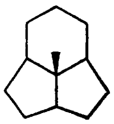
† Satisfactory spectral data were obtained for all new compounds.

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 ($t_{\frac{1}{2}}$ 12 h) to 2a-methyl-2a*H*-cyclopent[*cd*]-indene (**6**) by a [1,5]Me sigmatropic shift. The diester (**1**) rearranged similarly in xylene, with $t_{\frac{1}{2}}$ 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 2a*H*-isomer (**6**) is an oil, λ_{max} (EtOH) 258 (log ϵ 4·04), 318sh (2·50), and 331sh nm (2·41). The ^{1}H n.m.r. spectrum confirms the symmetrical nature of the 2a*H*-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 1*H*-isomers (**7**) and (**8**) by [1,5]-methyl and -hydrogen shifts. The unsubstituted 1*H*-isomer, 1*H*-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**).



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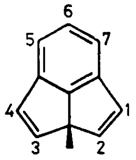

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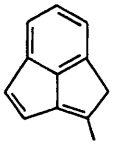

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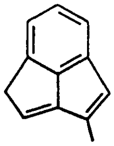

(8)

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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