J. CHEM. SOC., CHEM. COMMUN., 1983

5-Hydroxy-7b- methyl-7b*H*-cyclopent[*cd*]indene, a Stable Annulenol

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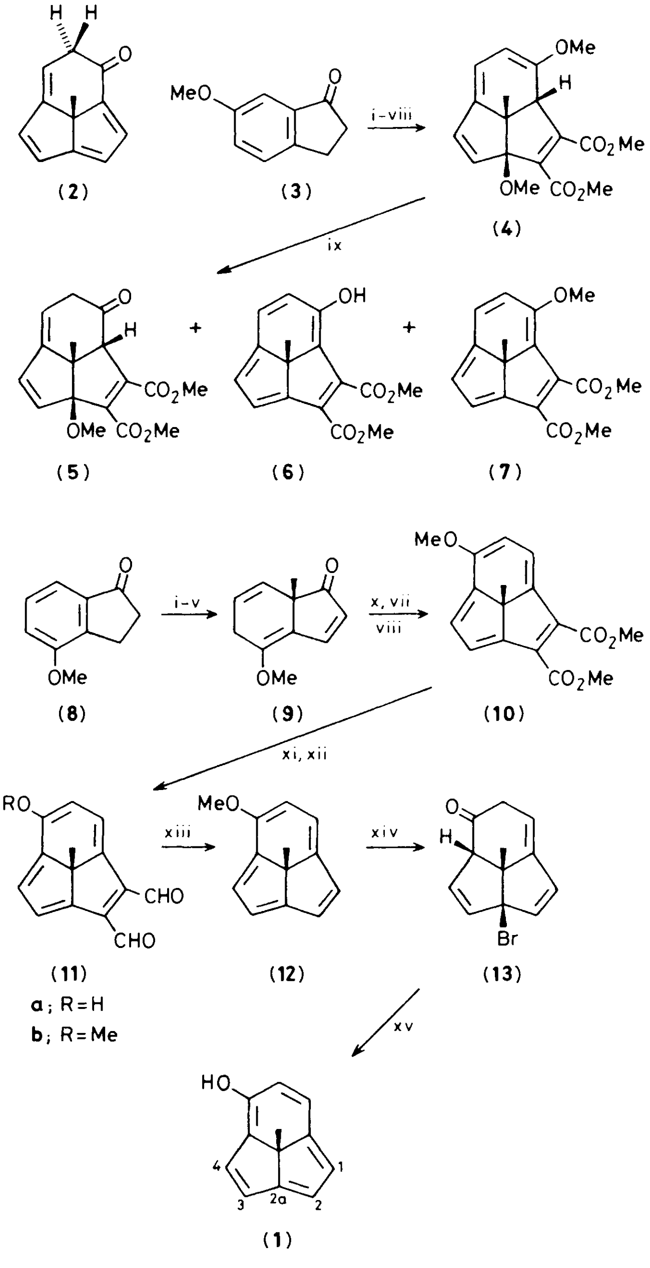
5-Hydroxy-7b-methyl-7b*H*-cyclopent[*cd*]indene (**1**), the diester (**6**), and dialdehyde (**11a**) exist in the stable enol form and are thus the first isolable higher annulenols.



Reagents: i, K, Bu^{t}OH, THF, LiBr, NH$_3$, −78 °C; ii, MeI, THF, NH$_3$, −78 °C; iii, LiNPr$^i_2$, THF, −78 °C; iv, PhSeCl, THF, −90 °C; v, H_2O_2, THF, pyridine, 0 to 5 °C; vi, KH, 18-crown-6, dimethoxyethane (DME); vii, MeOSO$_2$F; viii, MeO$_2$C–C≡C–CO$_2$Me; ix, H$_2$SO$_4$–MeOH; x, KH, KOH, 18-crown-6, DME, −20 °C; xi, LiAlH$_4$; xii, BaMnO$_4$; xiii, (PPh$_3$)$_3$RhCl; xiv, BBr$_3$; xv, DBU.

Greater stability of enol over keto forms resulting from π-electron delocalisation in annulenes higher than benzene has not hitherto been demonstrated. Previous attempts to isolate [10]annulenols[1,2] and a bisdehydro-[14]annulenol[3] were unsuccessful, and we recently found that 2-hydroxy-7b-methyl-7b*H*-cyclopent[*cd*]indene exists overwhelmingly in the keto form.[4] In the tricyclic [10]annulene, ring strain can be most effectively relieved by hydrogen shift to the 2a position, and with the 2-hydroxy isomer this occurs exclusively.[4] Since hydrogen shift to the 2a position is not possible with the 1- and 5-hydroxyannulenes, smaller energy differences between these isomers and their keto tautomers might be expected; indeed recent MNDO SCF-MO calculations suggest that the 5-hydroxy compound (**1**) could be more stable than its most stable keto tautomer (**2**),[5] and we now confirm this prediction by the synthesis of the stable annulenol (**1**), together with two ring-substituted derivatives (**6**) and (**11a**).

Initially we converted 6-methoxyindanone (**3**) into the cycloadduct (**4**) in 15% overall yield by a sequence of reactions described before.[6,7] On treatment with 1 : 1 concentrated sulphuric acid–methanol at 0 °C for 10 min, the cycloadduct (**4**) gave the (colourless) ketone (**5**) (40%), m.p. 108—109 °C, dimethyl 7-hydroxy-7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxylate (**6**) (15%) as deep-orange crystals, m.p. 83—84 °C, and its *O*-methyl ether (**7**) (8%) as an orange oil, δ(CDCl$_3$) −1.13 (7b-Me). On prolonged treatment under the same conditions the ketone (**5**) was slowly transformed into annulenol (**6**). The spectral properties of (**6**) were entirely consistent with the aromatic annulenol structure, showing no evidence for a keto form [ν_{max} (CHCl$_3$) 3 240 br., unaltered on dilution, 1665 cm^{-1};† ^{1}H n.m.r. (CDCl$_3$) δ −1.15 (s, 3H, 7b-Me), 4.01 (s, 3H), 4.07 (s, 3H), 7.26 (d, 1H, *J* 7.5 Hz), 7.72 (d, 1H, *J* 7.5 Hz), 8.01 (d, 1H, *J* 3.8 Hz), 8.04 (d, 1H, *J* 3.8 Hz), and 10.05 (s, 1H, OH)]. Since the intramolecular hydrogen bond to one ester group and the conjugative electron withdrawal by the other could markedly stabilise the enol form (**6**), it was important to synthesise the parent 5-hydroxy compound. As the yields of the possible precursors (**6**) and (**7**) were low this was done alternatively, as follows.

4-Methoxyindanone (**8**) was converted into the trienone (**9**) (35% overall) in the standard way.[6,7] Treatment of this trienone with an excess of potassium hydride in dimethoxyethane, containing potassium hydroxide and 18-crown-6 (1 equiv.), followed by methyl fluorosulphonate at −23 °C, and finally with dimethyl acetylenedicarboxylate at 40—60 °C gave the annulenediester (**10**) (65%) directly, as an orange oil, δ(CDCl$_3$) −1.19 (7b-Me). Diester (**10**) was converted into dialdehyde (**11b**) (65%), δ(CDCl$_3$) −1.07 (7b-Me), by reduction to the diol with lithium aluminium hydride followed by oxidation with barium manganate.[8] Ether (**11b**) was demethylated with boron tribromide in dichloromethane to give the hydroxy-dialdehyde (**11a**) (30%) as red crystals, m.p. 174—175 °C, δ(CDCl$_3$) −1.00 (7b-Me), and was decarbonylated by heating in benzene with tristriphenylphosphinerhodium(I) chloride for 9 h, followed by treatment with iodomethane and chromatography on silica gel, to give 5-methoxy-7b-methyl-7b*H*-cyclopent[*cd*]indene (**12**) (65%) as pale yellow waxy crystals, m.p. 12—14 °C; λ_{max}(EtOH) 464 nm (log ε 2.61);

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† This strong i.r. band shown by hydroxy compounds (**6**) and (**1**) but noticeably absent from the spectra of their methyl ethers (**7**) and (**12**), is assigned to enol C=C stretching.

δ(CDCl$_3$) −1.52 (s, 3H, 7b-Me), 4.23 (s, 3H, OMe), 7.11 (d, 1H, *J* 7.5 Hz), 7.62 (d, 1H, *J* 7.5 Hz), 7.66 (d, 1H, *J* 3.5 Hz), 7.77 (d, 1H, *J* 3.0 Hz), 7.79 (d, 1H, *J* 3.0 Hz), and 8.00 (d, 1H, *J* 3.5 Hz). The long-wavelength band is very close to that of the 2-methoxy isomer (459 nm, log ε 2.96)[4] supporting the absence of significant transannular homoaromatic interactions in the tricyclic, as opposed to the bicyclic, [10]annulenes (*cf.* ref. 9).

Attempted cleavage of ether (**12**) to the annulenol (**1**) with boron tribromide in dichloromethane for 15 min at −78 °C gave the bromotrienone (**13**). However, when this was stirred with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in dry benzene at room temperature for 30 min, work up with dilute aqueous sodium hydrogen sulphate and chromatography on silica gel gave 5-hydroxy-7b-methyl-7b*H*-cyclopent[*cd*]indene (**1**) [λ_{max}(EtOH) 293 (log ε 4.48), 326 sh (3.60), and 467 nm (2.54); ν_{max}(CCl$_4$), 3600, 1665 cm^{-1};† δ(CDCl$_3$) −1.49 (s, 3H, 7b-Me), 7.14 (d, 1H, *J* 7.1 Hz), 7.60 (d, 1H, *J* 7.1 Hz), 7.68 (d, 1H, *J* 3.0 Hz), 7.81 (d, 1H, *J* 3.2 Hz), 7.90 (d, 1H, *J* 3.2 Hz), and 7.95 (d, 1H, *J* 3.0 Hz)] as a yellow oil, stable in solution but which decomposes slowly at room temperature when neat, in 5% overall yield from 4-methoxyindanone (**8**). There was no spectroscopic evidence for a keto tautomer, and no deuterium was incorporated onto carbon when the annulenol was stored in D$_2$O–(CD$_3$)$_2$SO for one week. Furthermore, no *C*-methylation could be detected when the annulenol was treated with sodium hydride and lithium bromide in tetrahydrofuran (THF) followed by iodomethane which normally favour *C*- over *O*-methylation and under which conditions the 2-'hydroxy' isomer was exclusively methylated on carbon.[4] The u.v. spectrum of the annulenol (**1**) is very similar to that of its *O*-methyl ether, and the 2-methoxyannulene. Methanesulphonyl chloride in pyridine converted (**1**) into its methanesulphonate (45%), a yellow oil, δ(CDCl$_3$) −1.48 (7b-Me).

Thus, in the tricyclic [10]annulene series the 2-'phenol' which can tautomerise to the very stable 2a*H*-keto form exists in this keto form, whilst the 5-phenol which cannot, exists as the annulenol, as do the crystalline diester (**6**) and dialdehyde (**11a**). These appear to be the first higher annulenols stable enough to be isolated.

We thank Drs. C. J. Moody and H. S. Rzepa for valuable discussions and the Swedish Natural Science Research Council for a postdoctoral award.

Received, 4th January 1983; Com. 009

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