Synthesis and X-Ray Crystal Structure of (1*R*,11b*R*)-11b-Hydroxy-1,3-dimethyl-2,11b-dihydro-1*H*-cyclopenta[*l*]phenanthren-2-one

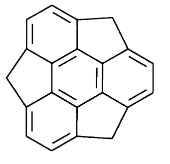
J. Chem. Research (S),
1997, 140–141
J. Chem. Research (M),
1997, 0977–0982

M. John Plater,* Derek M. Schmidt and R. Alan Howie

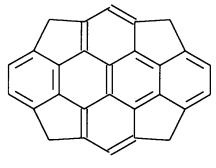
Department of Chemistry, Aberdeen University, Meston Walk, Aberdeen AB24 3UE, UK

The title compound was prepared by the condensation of phenanthraquinone with diethyl ketone and characterised by single-crystal X-ray crystallography.

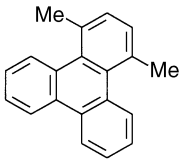
The cyclopenta-fused polycyclic active methylene compounds sumanene[1] **1** and pinakene[2] **2** and related derivatives are interesting strained target compounds which can be formally derived retrosynthetically from the buckminsterfullerene surface. They are also anticipated to be useful intermediates for further buckybowl fragment synthesis *via* functionalisation of the active methylene groups.[3] The strained core will also help to ensure a gradual increase in strain energy for successive endothermic ring couplings around the periphery. As part of a programme aimed at their synthesis from appropriate polycyclic precursors we wished to prepare 1,4-dimethyltriphenylene **3** from phenanthraquinone **4** and related compounds.



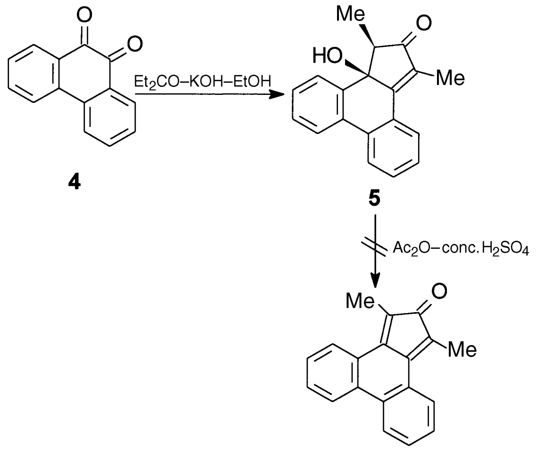
1



2



3



4

5

6

Treatment of phenanthraquinone **4** with diethyl ketone and potassium hydroxide at room temperature gave colourless crystals of the expected addition product **5**. However, in contrast to the facile generation of many cyclopentadienones derived from related 1,2-diketones,[4] we were unable to dehydrate **5** to the cyclopentadienone **6**. Treatment with a catalytic amount of sulfuric acid in acetic anhydride gave deep red coloured solutions but the cyclopentadienone or the expected dimer could not be isolated. *In situ* interception with dimethyl acetylenedicarboxylate or norbornadiene was also unsuccessful.

The structure of the adduct **5** was supported by spectroscopic data but, owing to the failure to dehydrate it and the potential for phenanthraquinone to undergo a benzilic acid ring contraction, a confirmatory single-crystal X-ray structure determination was performed (see Fig. 1). The compound crystallises as a racemate and forms extended chains with an intermolecular hydrogen bond from the hydroxy group O(1) to the ketone carbonyl group O(2). The methyl group C(18) and hydroxy group O(1) are *cis*, as opposed to the thermodynamically more stable *trans* arrangement, which will be a consequence of the preferred formation of the *Z*-enolate prior to ring closure. Presumably the *Z*-enolate **7** forms exclusively as opposed to the *E*-enolate **8**, owing to the unfavourable steric interactions of the methyl group in the *E* enolate as shown.

Crystal Data for **5**.—$C_{19}H_{16}O_2$, $M_r = 276$, $F(000) = 584$, monoclinic, $a = 7.834(6)$, $b = 16.172(109)$, $c = 11.252(10)$ Å, $\beta = 92.50(7)°$, $V = 1424$ Å^3, space gorup $P2_1/c$ (No. 14), $Z = 4$, $D_r = 1.289$ gcm^{-3}, $\mu(\text{MoK}\alpha) = 0.063$ mm^{-1}. The experimental data were collected at room temperature on a Nicolet P3 diffractometer using a graphite monochromator with MoKα radiation ($\lambda = 0.71069$ Å). The structure was solved by direct methods.[5] The final R value was 0.058 ($R_w = 0.060$). The estimated standard deviations for the geo-

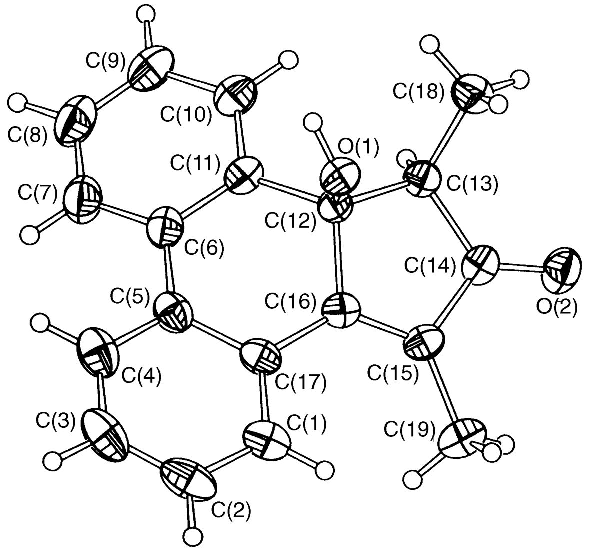
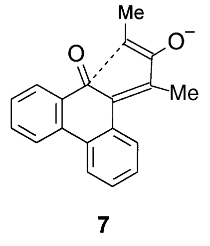
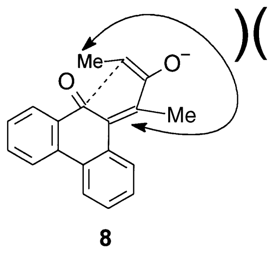


Fig. 1 X-Ray crystal structure of **5**



7
Preferred enolate



8

---

*To receive any correspondence.

metrical parameters involving non-hydrogen atoms lie within the following ranges: bond lengths 0.002–0.003 Å; bond angles 0.14–0.2°.

Alternative methods to synthesise precursors to sumanene and pinakene are in progress.

Techniques used: IR, ^{1}H NMR, X-ray diffraction

References: 10

Table 1: Atomic coordinates and U_{eq} values for **5**

Table 2: Interatomic distances and angles, hydrogen bond distances and angles, and selected dihedral angles

Received, 4th December 1996; Accepted, 10th January 1997
Paper E/6/08201G

References cited in this synopsis

1 G. Mehta, E. D. Jemmis and G. Narahari Sastry, *J. Chem. Soc., Perkin Trans. 2*, 1994, 437.
2 G. Mehta, G. N. Sastry, E. L. Jemmis and S. R. Shah, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1867.
3 M. J. Plater, M. Praveen and D. M. Schmidt, *Fullerene Science and Technology*, in press.
4 M. A. Ogliaruso, M. G. Romanelli and E. I. Becker, *Chem. Rev.*, 1965, **65**, 261.
6 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.