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## Key indicators

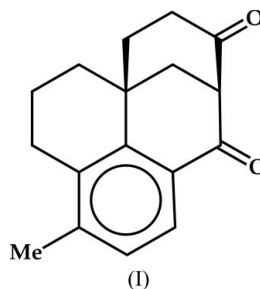
Single-crystal X-ray study  
 $T = 296\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$   
 $R$  factor = 0.051  
 $wR$  factor = 0.132  
Data-to-parameter ratio = 14.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**(±)-2,3,3a,4,5,6-Hexahydro-7-methyl-1,12-dioxo-  
2,3a-propanophenalene: a new four-ring carbocyclic  
system**

The title racemate,  $\text{C}_{17}\text{H}_{18}\text{O}_2$ , is a tetracyclic diketone isolated from the base-catalysed Robinson annulation of 2-(2-carbethoxyethyl)cyclohexanone. It represents a previously unreported four-ring carbocyclic system. In the crystal structure, the packing includes three close intermolecular  $\text{C}-\text{H}\cdots\text{O}$  dipolar contacts, involving both ketones.

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## Comment

An interest in keto acids containing the naphthalene skeleton led us to study the Robinson annulation of several 2-substituted cyclohexanones, utilizing a variety of base and acid catalysts (Zewge *et al.*, 1998; Davison *et al.*, 2004). One such reaction, employing 2-(2-carbethoxyethyl)cyclohexanone, methyl vinyl ketone (MVK) and sodium methoxide, provided a low yield of an unknown crystalline material, (I), that was neutral and resisted saponification. X-ray crystallography established the structure of (I).



Compound (I) evidently arises from a normal Robinson annulation of our starting material at the more highly substituted carbon (House, 1972), followed by Michael condensation with a second molecule of MVK at the newly created enone's  $\alpha$  position and a subsequent ring closure originating from the same enone's  $\gamma$  position. This substituted phenalene system then requires an oxidation from some source, possibly air, to aromatize the methylated ring. Attachment of the second molecule of MVK in the reverse sense, leading to a 9-methylated product, is an imaginable but unobserved outcome. This double condensation occurs despite a significant insufficiency of MVK; however, the recovered yield of (I) was extremely low (see *Experimental*). At some point, necessarily after the enone formation, an internal Claisen condensation also creates the oxopropane bridge. The only diastereomers possible are the two enantiomers present.

Within the  $2.7\text{ \AA}$  range we surveyed for non-bonded  $\text{C}-\text{H}\cdots\text{O}$  packing interactions (Steiner, 1997); three close intermolecular contacts were found, involving both ketones (Table 1, Fig. 2).

Experimental

Compound (I) was isolated from a reaction in which 41 mmol of ethereal MVK was added slowly to a cold methanolic solution of 50 mmol of 2-(2-carboxyethyl)cyclohexanone and 67 mmol of sodium methoxide. Overnight stirring, heating with water and the usual workup led to a 1.1% yield of (I), isolated from the highest boiling of three distillation fractions. The reactions, but not the isolative manipulations, were carried out under N<sub>2</sub>. Crystals suitable for X-ray analysis were produced from acetone–hexane, m.p. 462 K.

Crystal data

C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>  
M<sub>r</sub> = 254.31  
Monoclinic, P2<sub>1</sub>/n  
a = 7.9630 (12) Å  
b = 13.526 (2) Å  
c = 12.159 (2) Å  
β = 96.240 (11)°  
V = 1301.9 (3) Å<sup>3</sup>  
Z = 4

D<sub>x</sub> = 1.298 Mg m<sup>-3</sup>  
Mo Kα radiation  
Cell parameters from 24 reflections  
θ = 3.1–8.2°  
μ = 0.08 mm<sup>-1</sup>  
T = 296 (2) K  
Parallelepiped, colourless  
0.50 × 0.34 × 0.20 mm

Data collection

Siemens P4 diffractometer  
ω/2θ scans  
Absorption correction: numerical (SHELXTL; Sheldrick, 1997)  
T<sub>min</sub> = 0.964, T<sub>max</sub> = 0.985  
3394 measured reflections  
2555 independent reflections  
1501 reflections with I > 2σ(I)

R<sub>int</sub> = 0.034  
θ<sub>max</sub> = 26.0°  
h = -1 → 9  
k = -16 → 1  
l = -14 → 14  
3 standard reflections every 97 reflections  
intensity decay: <2.3%

Refinement

Refinement on F<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.051  
wR(F<sup>2</sup>) = 0.132  
S = 1.01  
2555 reflections  
172 parameters  
H-atom parameters constrained

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0531P)<sup>2</sup> + 0.1948P]  
where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
(Δ/σ)<sub>max</sub> < 0.001  
Δρ<sub>max</sub> = 0.20 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.17 e Å<sup>-3</sup>

Table 1

Close contact geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C8—H8...O1 <sup>i</sup>	0.96	2.61	3.543 (3)	163
C10—H10B...O1 <sup>ii</sup>	0.97	2.58	3.440 (3)	148
C11—H11A...O2 <sup>iii</sup>	0.97	2.61	3.557 (3)	167

Symmetry codes: (i) -x + ½, y + ½, -z + ¾; (ii) x + ½, -y + ¾, z - ½; (iii) -x + 1, -y + 1, -z + 1.

All H atoms were located in electron density difference maps but were placed in calculated positions with C—H = 0.96–0.98 Å and allowed to refine in a riding-model approximation with U<sub>iso</sub>(H) = 1.2U<sub>eq</sub>(C) or 1.5U<sub>eq</sub>(C) for methyl H atoms.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

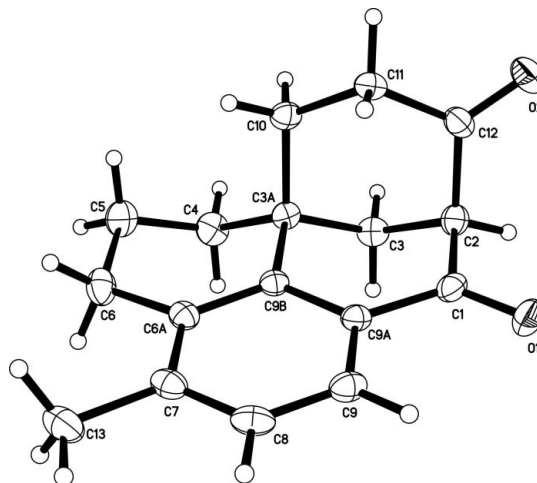


Figure 1 A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 20% probability level.

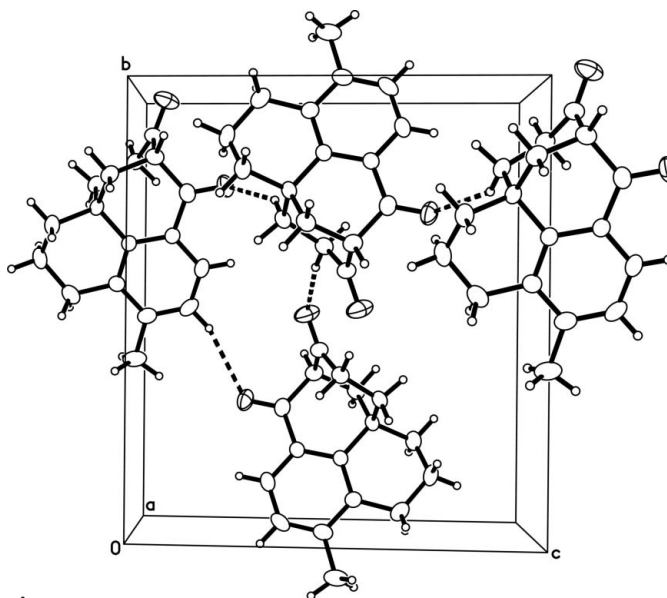


Figure 2 Packing diagram for (I), with displacement ellipsoids drawn at the 20% probability level. Close contacts are shown as dashed lines

References

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