

The Ozonolysis of α -Terpineol – Unusual Formation of a 6,6-Dimethylfulvene Epoxide

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Dedicated to Professor Albert Eschenmoser on the occasion of his 60th birthday

Abstract: Ozonolysis of α -terpineol (**1**) followed by steam distillation in the presence of acid is known to give 4-isopropylidenecyclopentenyl methyl ketone (**3**). In the absence of light, the latter is oxidized by air to the 4-(1-hydroperoxy-1-methylethyl)-1,3-cyclopentadien-1-yl derivative **4**. On silica gel this compound formed two possible dimers (**5**, **6**) of 3-acetyl-6,6-dimethylfulvene epoxide, the structures of which were established by X-ray crystallography. This work establishes by analogy, the stereochemistry of dimethylfulvene epoxide dimers previously described.

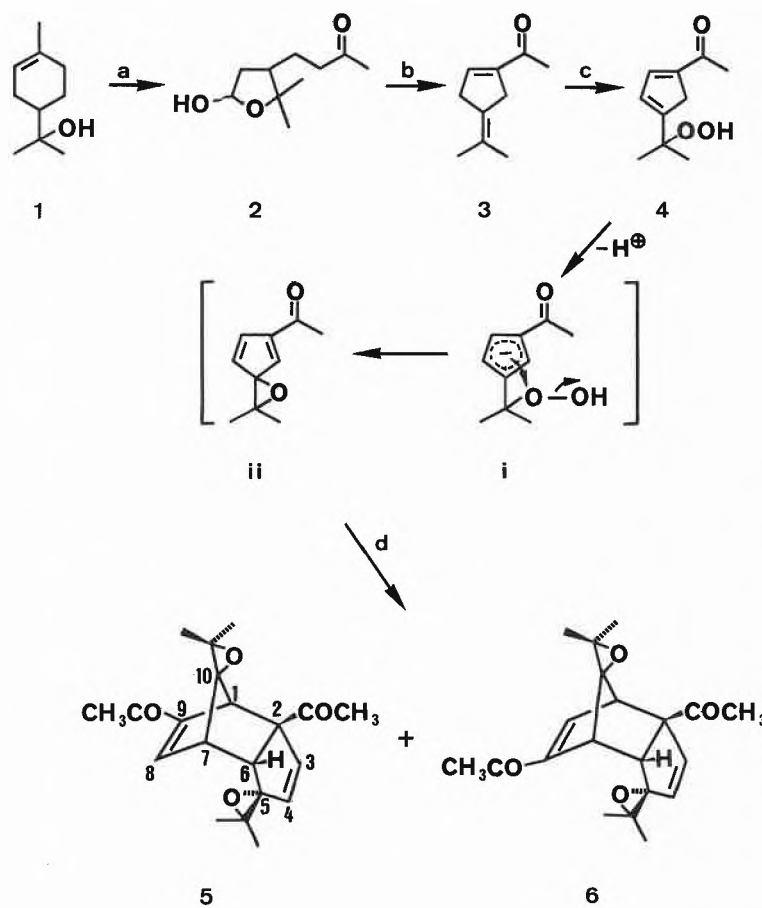
Ozonolysis of α -terpineol **1**, followed by steam distillation of the initially formed lactol **2** has been reported in a brief note to give the 4-isopropylidenecyclopentenyl methyl ketone **3**^[1]. This crystalline ketone (*m.p.* 76–78°C), after standing for three days in air in the dark, gave a different crystalline substance with *m.p.* 82–84°C. The latter contained a conjugated methyl ketone (IR spectrum (CHCl₃): $\nu_{C=O}$ = 1645 cm⁻¹), two olefinic protons (AB system, δ = 6.51 and 7.29, J = 2 Hz^[2]), a CH₂ group (δ = 3.42), and had a peroxide index of 71,845. This was ascribed structure **4**, and thin-layer chromatography in hexane-ether (8:2) revealed two spots. Chromatography of the hydroperoxide in pentane-ether (1:1) on silica gel enabled two isomers corresponding to the two spots to be isolated as crystals, the less polar isomer having *m.p.* 138°C, and the more polar isomer *m.p.* 152°C. The structures of the two isomers were determined by X-ray crystallography (see table 2) as **5** (for the less polar isomer) and **6** (the more polar). They were also characterized spectrally; in particular, the ¹H-NMR spectra exhibited the chemical shifts shown in table 1. Notable are the coupling constants of the protons on C-1 and C-7. In the case of isomer **5**, the proton on C-1 has only a long-range coupling (1.5 Hz with that on C-6) and the

proton on C-7 has two vicinal couplings (4.5 Hz with the proton on C-6 and 3 Hz with the proton on C-8), while in isomer **6** both the bridgehead protons have a vicinal coupling (3.5 Hz for the one at C-1 and 4 Hz for C-7) and a long-range coupling (1.5 Hz in both cases).

Table 1. Chemical shifts (δ values) in the ¹H-NMR spectra of the two isomeric compounds **5** and **6**.

	proton on						
	C-1	C-3	C-4	C-6	C-7	C-8	C-9
5	3.66	5.91	5.51	2.71	3.65	7.11	–
6	3.43	5.78	5.63	3.02	3.48	–	6.80

Formation of these dimeric compounds presumably is triggered by the extreme acidity of a proton of the methylene group in **4**. The cyclopentadienyl anion **i** resulting from its loss can be stabilized by loss of hydroxide to the dimethylfulvene epoxide **ii**. The latter are known to dimerize immediately^[3]. The first example of this dimerization, from unsubstituted dimethylfulvene epoxide, was quoted without stereochemistry^[3]. Our results clearly show that



a: O₃, P(OCH₃)₃

b: H₃PO₄, steam distillation

c: air

d: silica gel

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approach of a second molecule of epoxide must take place from the epoxide side only, so that the products will in general be the *endo*, *syn* diepoxides. Further examples of alkyl methyl fulvene epoxide dimers have been given by Näf et al.^[4] and these too must be *endo*, *syn* isomers.

The atomic coordinates for this work have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. Observed and calculated structure factors may be obtained from one of the authors (G.B.) upon request.

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Table 2. Crystal data from the dimethylfulvene epoxide dimers **5** and **6**.

5: C₂₀H₂₄O₄, $M_r = 328.4$; monoclinic, space group P2₁/n; $a = 13.100$ (3), $b = 8.6517$ (11), $c = 15.805$ (3) Å; $\beta = 93.69$ (2)°; $Z = 4$; $\mu = 0.784$ cm⁻¹; $F_{000} = 704$; $\rho_c = 1.220$ g·cm⁻³; $R = 0.044$ for 1193 observed reflections ($|F_o| \geq 3\sigma(F_o)$ and $|F_o| \geq 7.0$).

6: C₂₀H₂₄O₄, $M_r = 328.4$; orthorhombic, space group P2₁2₁2₁; $a = 6.9764$ (17), $b = 14.892$ (2), $c = 17.043$ (5) Å; $Z = 4$; $\mu = 0.791$ cm⁻¹; $F_{000} = 704$; $\rho_c = 1.232$ g·cm⁻³; $R = 0.055$ for 1134 observed reflections ($|F_o| \geq 4\sigma(F_o)$).

Both crystals were measured at room temperature on a Philips PW1100 diffractometer with graphite monochromated MoK α radiation. The structures were solved by direct methods^[5] and refined by full-matrix techniques^[6]. All the coordinates of the hydrogen atoms were calculated.

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