

Photochemical Oxidation of Benzyl Alcohol. Correction of Reported Structures

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A few years ago Erra Balsells and Frasca reported on the photochemical reactions of aromatic alcohols.¹ From the irradiation of benzyl alcohol they claim to have obtained, among other products, the two isomeric 2,3,5,6-tetraphenyl-1,4-dioxanes **1a** and **1b**. Our attention to this work was drawn from a recent paper by Hansen and Sydnes who were unable to reproduce the results.² The structures assigned to these isomers were based on spectral data. The presence of an ion at m/z 392 of 1% abundance in the EI-MS spectrum of **1a** was assumed by the authors to be the ion corresponding to the molecular formula $C_{28}H_{24}O_2$. The same compound gave rise to a complex absorption in the 1H NMR spectrum at about δ 7–8, and two singlets at δ 4.97 and 6.42 in a ratio of 2:1. The second isomer was assigned the structure **1b** on similar data, but the m/z 392 peak was absent in this case. Moreover, the conclusion that the 1H NMR spectrum of each of the isomers **1** resulted from a mixture of two conformers in solution at room temperature was not convincing. On the other hand, the presence in the reaction product of *meso*- and (\pm)-1,2-diphenyl-1,2-ethanediol as well as benzaldehyde was established by comparison with authentic samples. Their photochemical formation from benzyl alcohol was expected, having precedence in the literature.³

It occurred to us that the spectral data reported for the isomers **1** would be quite consistent with those expected for

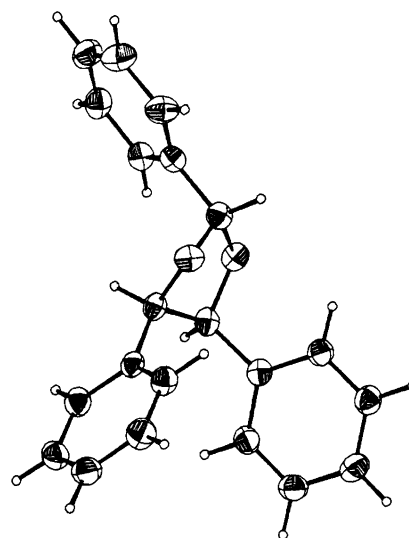
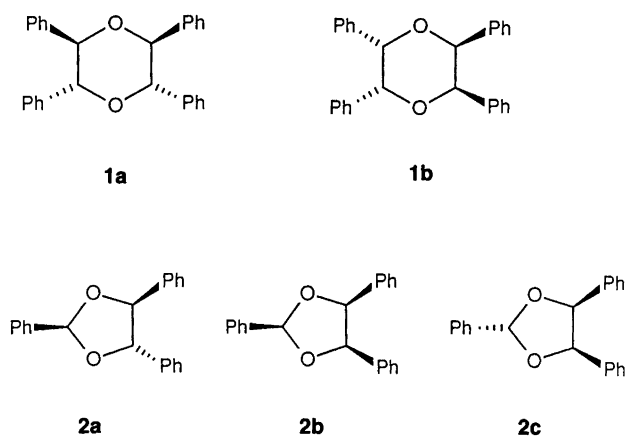


Fig. 1. ORTEP plot of $C_{21}H_{18}O_2$ (**2c**).

the triphenyl-1,3-dioxolanes **2a–2c**. Consequently we prepared the acetal **2a**, m.p. 84°C, in 90% yield from benzaldehyde and (\pm)-1,2-diphenyl-1,2-ethanediol.^{4,5} The 1H NMR spectrum was indeed identical with that reported by Erra Balsells and Frasca for **1a**. The major peaks in the mass spectra are the same as well; the additional peaks in the published spectrum we assume are due to impurities which are indicated by the low melting point. A similar reaction using the *meso*-diol gave in 89% yield an approximately 3:2 mixture of the isomeric acetals **2b** and **2c**, which were separated by flash chromatography on silica gel. The major component **2b**, m.p. 99°C, exhibited spectral properties almost identical with those reported for **1b**. We believe that also in this case the minor discrepancies in the mass spectra are caused by contaminations in the published sample. The minor component **2c**, m.p. 110°C,⁶ gave rise to singlets at δ 5.43 and 6.83 in a 2:1 ratio, due to the benzylic and acetal protons, respectively, and surprisingly it does not seem to be present in the published samples.¹ These isomers had not been separated previously, but from the 1H NMR spectrum of the mixture the configuration **2c** was assigned to the high-melting and minor isomer based

on chemical shift arguments.⁷ Although we could not disagree with this conclusion it still seemed surprising that this reaction should produce as the major product the thermodynamically least stable isomer; from molecular mechanics calculations **2c** is more stable by 14 kJ mol⁻¹. The configuration of the latter was therefore determined by X-ray crystallography, which confirmed the original assignment (Fig. 1).

Hence we must conclude that the photochemical reaction of benzyl alcohol does not yield the tetraphenyldioxanes **1** as claimed, but isomers of 2,4,5-triphenyl-1,3-dioxolane (**2**), among other products. It seems reasonable that under the conditions used by Erra Balsells and Frasca the dioxolanes resulted from dark reactions of photochemically produced starting materials.

Experimental

The IR spectra were recorded on a Perkin Elmer 1310 spectrometer. The ¹H NMR spectra were obtained on JEOL PMX 60si and the mass spectra on Micromass 7070 F instruments. The MM2 calculations were carried out using the Alchemy II program.

2,4,5-Triphenyl-1,3-dioxolane (2a). A solution of (±)-1,2-diphenyl-1,2-ethanediol (0.36 g, 1.68 mmol) and benzaldehyde (0.20 g, 1.88 mmol) in benzene (30 ml), containing some crystals of *p*-toluenesulfonic acid and connected to a Dean-Stark trap, was heated under reflux for 1 h. Recrystallisation of the crude product gave **2a** (0.46 g, 90%) as colourless needles from heptane, m.p. 84°C (lit.⁴ 84°C, lit.⁵ 82–84°C). IR (CCl₄): 1720, 1090, 1060, 1020, 1000, 690 cm⁻¹. ¹H NMR (60 MHz, CDCl₃): δ 4.93 (s, 2 H), 6.41 (s, 1 H), 7.20–7.83 (m, 15 H). MS (EI 70 eV): *m/z* 196 (100), 195 (30), 178 (22), 167 (63), 165 (12), 152 (7), 105 (27), 90 (45), 89 (37), 77 (29), 63 (8), 51 (16).

2,4,5-Triphenyl-1,3-dioxolane (2b and 2c). The reaction of benzaldehyde with *meso*-1,2-diphenyl-1,2-ethanediol as described for **2a** gave a 3:2 mixture of isomers **2b** and **2c** in 89% yield. The isomers were separated by flash chromatography (silica gel, petroleum ether/EtOAc 97.5:2.5) and recrystallised from hexane.

Major isomer **2b**: m.p. 99°C. IR (CCl₄): 1720, 1450, 1220, 1090, 1060, 1030, 1010, 700 cm⁻¹. ¹H NMR (60 MHz, CDCl₃): δ 5.50 (s, 2 H), 6.18 (s, 1 H), 7.00–7.86 (m, 15 H). MS (EI 70 eV): *m/z* 196 (100), 195 (30), 178 (22), 167 (63), 165 (12), 152 (7), 105 (27), 90 (45), 89 (37), 77 (29), 63 (8), 51 (16).

Minor isomer **2c**: m.p. 110°C (lit.⁶ 109–110°C). IR (CCl₄): 1720, 1500, 1450, 1210, 1100, 1070, 1020, 700 cm⁻¹. ¹H NMR (60 MHz, CDCl₃): δ 5.43 (s, 2 H), 6.83 (s, 1 H), 7.03–7.86 (m, 15 H). MS (EI 70 eV): *m/z* 196 (100), 195 (35), 178 (21), 167 (63), 165 (12), 152 (7), 105 (21), 90 (42), 89 (34), 77 (25), 63 (8), 51 (13).

Table 1. Crystal and experimental data for 2,4,5-triphenyl-1,3-dioxolane (**2c**).

Compound	C ₂₁ H ₁₈ O ₂
Melting point	110°C
Diffractometer	NICOLET P3/F
Crystal size/mm	0.5×0.4×0.1
Radiation	MoK _α (λ = 0.71069 Å)
Crystal system	Monoclinic
<i>a</i> /Å	11.807(2)
<i>b</i> /Å	5.910(1)
<i>c</i> /Å	22.190(3)
β/°	94.89(2)
<i>V</i> /Å ³	1542.8(5)
Temp./°C	135
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>M</i>	302.37
<i>Z</i>	4
<i>F</i> (000)	640
<i>D_x</i> /g cm ⁻³	1.302
μ (MoK _α)/cm ⁻¹	0.77
Scan mode	θ/2θ
Scan speed (2θ° min ⁻¹)	4
Scan range (2θ°)	1.9
Maximum sinθ/Å ⁻¹	0.75
No. of indep. meas.	5170
No with <i>I</i> > σ(<i>I</i>)	3261
Correction for absorption	Empirical
Method to solve structure	Mithril
No. of parameters refined	280
<i>R</i> = Σ <i>F_o</i> - <i>F_c</i> /Σ <i>F_o</i>	0.044
<i>R_w</i> = [Σ <i>w</i> (<i>F_o</i> - <i>F_c</i>) ² /Σ <i>wF_o</i> ²] ^{1/2}	0.044
<i>S</i> = [Σ <i>w</i> (<i>F_o</i> - <i>F_c</i>) ² /(<i>n</i> - <i>m</i>)] ^{1/2}	2.25

X-Ray structure determination of isomer 2c. Large needles were obtained on recrystallisations from hexane. Crystal and experimental data are given in Table 1. Three test reflections were measured periodically at intervals of 135 reflections during the intensity data collection; a small systematic variation was observed and the data were adjusted accordingly. Corrections were made for Lorenz and polarisation effects. Unit cell dimensions were determined from diffractometer setting angles for 25 reflections. The coordinates of all non-hydrogen atoms were determined by direct methods.⁸ Refinements were performed by least-squares calculations; hydrogen atom positions were calculated and included in the refinements. An empirical absorption correction was applied,⁹ and the least-squares calculations proceeded with anisotropic temperature factors for the non-hydrogen atoms. Computer programs employed are described in the literature.¹⁰ Final figures of merit are included in Table 1. Positional parameters and structure factors may be obtained from the authors upon request.

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