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Photochemical Reaction of β-Hydroxyketones. Formation of Cyclopropane-1,2-diols

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Irradiation of 3-hydroxy-1-(*o*-methylaryl)-2,2,4-trimethylpentan-1-ones **1** in methanol gave cyclopropane-1,2-diols **2**, 1,3-diketones **3** and benzocylobutenols **4**.

It is known that irradiation of aryl ketones containing *ortho*-alkyl groups produces the triplet states of enols, which generally revert to the starting materials in the dark.[1] We have recently reported that 1-(*o*-methylphenyl)-2,2-dimethyl 1,3-diketones underwent photocyclization to give benzocyclobutenols because the reverse transfer of hydrogen in the intermediate diradicals to reproduce the starting ketones was suppressed owing to intramolecular hydrogen bonding.[2] Because of our interest in the effect of β-functional groups on the photoreactivity of ketones, we studied the photochemistry of 3-hydroxy-1-(*o*-methylaryl)-2,2,4-trimethylpentane-1-ones **1**, and found a novel reaction to yield cyclopropane-1,2-diols **2**, along with 1,3-diketones **3** and benzocyclobutenols **4**.

Irradiation of a methanol solution (160 ml) of the ketone **1a** (600 mg) with Pyrex-filtered light and ice-cooling gave two isomeric cyclopropanediols *trans*-**2a** (m.p. 100–101 °C, 16%) and *cis*-**2a** (m.p. 117–119 °C, 9%). Their structures were elucidated on the basis of analytical and spectral data. Their IR spectra showed hydroxy and no carbonyl absorptions. The ^{1}H NMR spectrum (400 MHz, in $CDCl_3$; *J* values in Hz) showed two hydroxy groups (*trans*-**2a**: δ 1.42 and 1.69; *cis*-**2a**: δ 2.48 and 2.53), an arylmethyl group (*trans*: δ 2.38; *cis*: δ 2.39), an isopropyl group [*trans*: δ 1.05 (3H, d, *J* 7), 1.22 (3H, d, *J* 7) and 2.28 (1H, sept, *J* 7); *cis*: δ 1.08 (3H, d, *J* 7), 1.37 (3H, d, *J* 7) and 1.89 (1H, sept, *J* 7)], two methyl groups (*trans*: δ 0.92 and 1.32; *cis*: δ 0.83 and 1.24), and four aromatic protons (*trans*: δ 7.1–7.4; *cis*: δ 7.1–7.4). Their configurations were established by cyclic esterification using phenylboronic acid. Compound *cis*-**2a** reacted with phenylboronic acid to give the ester as an oil [^{1}H NMR (400 MHz, in $CDCl_3$; *J* values in Hz): δ 0.86 (3H, s), 1.11 (3H, s), 1.24 (3H, d, *J* 7), 1.39 (3H, d, *J* 7), 2.12 (1H, sept, *J* 7), 2.45 (3H, s) and 7.1–7.9 (9H, m)] while *trans*-**2a** did not react. When carbon tetrachloride solutions of both *trans*-**2a** and *cis*-**2a** were left at room temperature for 45 days, they were converted quantitatively to the diketone **3a**. It is known that solutions of cyclopropane-1,2-diols are readily oxidized to 1,3-diketones by oxygen in the air.[3] Irradiation of the hydroxy-ketone **1b** under the same conditions gave two isomeric cyclopropane-1,2-diols *trans*-**2b** (m.p. 111–112 °C, 27%) and *cis*-**2b** (m.p. 114 °C, 10%), along with the 1,3-diketone **3b** and two isomeric benzocyclobutenols **4b**† (m.p. 136 °C, 11%; m.p. 95 °C, 10%). Irradiation of the hydroxy-ketone **1c** under the same conditions gave the *trans*-cyclopropane-1,2-diol **2c** (m.p. 93–94 °C, 28%), the 1,3-diketone **3c**, and the benzocyclobutenol **4c**† (m.p. 96–97 °C, 13%).

Cyclopropane-1,2-diols were postulated as intermediates in the Clemmensen reduction of 1,3-diketones, and such species have been trapped as diacetates.[4] However, there are few reprots on the preparation of free cyclopropane-1,2-diols; methods include the electrochemical reduction of 1,3-diketones[5] and their reduction[3a] using alkali metal in liquid ammonia.

Photolysis of ketones having hydrogen atoms on both β- and γ-carbon atoms leads preferentially to abstraction of the latter.[6] The formation of benzocylobutenols **4** can be reasonably explained in terms of γ-hydrogen abstraction from the arylmethyl group by the carbonyl oxygen followed by cyclization of the resulting diradicals. The cyclopropane-1,2-diols **2** may be cyclization products involving β-hydrogen abstraction. When 3-hydroxy-2,2,4-trimethyl-1-phenylpentan-1-one was irradiated under the same conditions, 2,2,4-trimethyl-1-phenylpentane-1,3-dione was obtained in 17% yield, though the corresponding cyclopropane-1,2-diol could not be obtained. This cyclopropane-1,2-diol is probably so sensitive

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† The configurations of these compounds could not be assigned.

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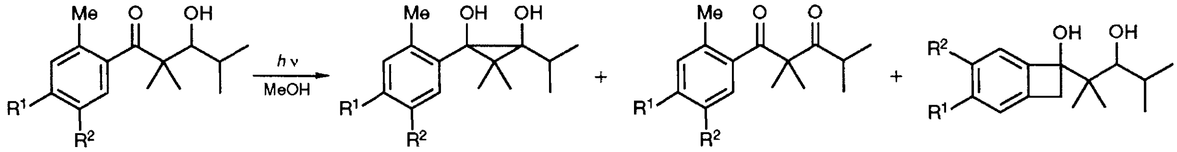

1 **2** **3** **4**

a; R^1=R^2=H **b**; R^1=H, R^2=Me **c**; R^1=Me, R^2=H

to air that it is rapidly oxidized to give the 1,3-diketone. Therefore, the formation of **2** can be rationalized in terms of the abstraction of hydrogen on C(3) which is activated by the hydroxy group, followed by cyclization of the resulting 1,3-diradical.

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