

## Photochemical Reaction of *o*-Alkylphenyl 1,3-Diketones. A New Method for the Preparation of Benzocyclobutenones

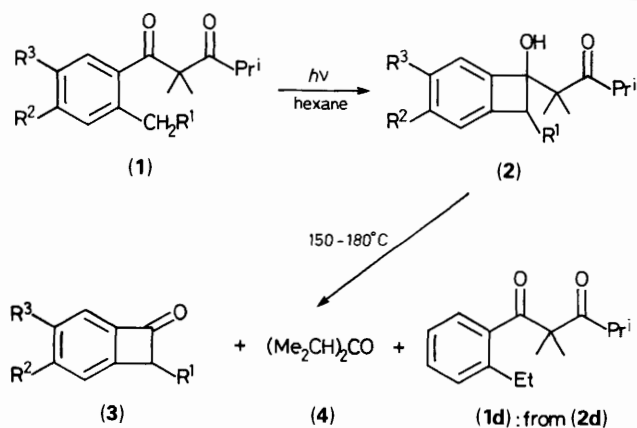
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Irradiation of *o*-alkylphenyl 1,3-diketones (1) in hexane gave benzocyclobutenols (2) which underwent thermal retro-aldol cleavage to yield benzocyclobutenones (3).

The photochemistry of *o*-alkylphenylketones has been extensively studied.<sup>1</sup> In these ketones, the carbonyl oxygen of the  $n, \pi^*$  triplet state abstracts hydrogen from the  $\alpha$ -carbon of the *o*-alkyl group to produce a triplet diradical (a triplet state of the enol<sup>2</sup>), which decays both to the enol and the starting ketone ground state.<sup>†</sup> The ground state enol is normally a short-lived species at ambient temperature and undergoes a rapid reketonization. The *o*-alkylphenyl 1,3-diketones (1) are expected to give benzocyclobutenols (2) on irradiation because the reverse transfer of hydrogen in the diradical intermediates to reproduce the starting ketones may be suppressed owing to intramolecular hydrogen bonding,<sup>3</sup> and the resulting benzocyclobutenols may undergo retro-aldol cleavage to yield benzocyclobutenones (3). Benzocyclobutenone and its derivatives have been of much interest in



a: R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H

b: R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = Me

c: R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = Me

d: R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H

<sup>†</sup> The highly hindered aromatic ketones such as 2,4,6-trialkylphenylketones yield benzocyclobutenols *via* a diradical process because the enol is more hindered than the benzocyclobutenols.<sup>6</sup>

synthesis.<sup>4</sup> We report here that *o*-alkylphenyl 1,3-diketones (**1**) undergo photocyclization to give benzocyclobutenols (**2**) and that (**2**) undergo thermal retro-aldol cleavage to yield benzocyclobutenones (**3**).

Irradiation of a hexane solution (120 ml) of 1-(*o*-methylphenyl)-2,2,4-trimethylpentane-1,3-dione (**1a**) (600 mg) with Pyrex-filtered light gave the benzocyclobutenol (**2a**) (m.p. 37 °C, 45%).<sup>‡</sup> The structure of (**2a**) was assigned on the basis of analytical and spectral data. The <sup>1</sup>H NMR spectrum showed an AB-quartet ( $\delta$  3.04, 3.38, *J* 14 Hz) due to the two methylene protons of the four-membered ring. The IR spectrum showed hydroxy (3600 and 3500 br. cm<sup>-1</sup>) and carbonyl (1700 cm<sup>-1</sup>) absorptions. The carbonyl band appeared at rather lower wave number than normal alkyl ketones because of the intramolecular hydrogen bonding. It is known that the photoenolization of *o*-alkylphenylketones occurs highly efficiently and that reketonization to the starting materials is very fast at room temperature. The facile formation of (**2a**) from (**1a**) can be rationalized by intramolecular hydrogen bonding retarding the reketonization of the diradical to the starting ketone.

The benzocyclobutenol (**2a**) readily underwent retro-aldol cleavage, probably through a six-membered cyclic mechanism. When (**2a**) was heated in a sealed glass tube at 150 °C for 3 h and the mixture was analysed by <sup>1</sup>H NMR, the quantitative formation of benzocyclobuten-1(2*H*)-one (**3a**)<sup>4a</sup> and 2,4-dimethylpentan-3-one was observed. The benzocyclobutenone (**3a**) was separated by GC and identified by its spectral data. When *o*-alkylphenyl 1,3-diketones (**1b–d**) were irradiated under the same conditions as (**1a**), the corresponding benzocyclobutenols (**2b–d**) (oils, 44–60%) were obtained. Pyrolysis of (**2b**) and (**2c**) at 170–180 °C gave the corresponding benzocyclobutenones, (**3b**) (m.p. 51 °C) and (**3c**)<sup>4b</sup> (m.p.

46 °C), and 2,4-dimethylpentan-3-one quantitatively. In contrast to (**2a–c**), pyrolysis of (**2d**) at 180 °C gave mainly the starting ketone (**1d**) along with a small amount of the benzocyclobutenone (**3d**) [(**1d**):(**3d**) 9:1] and 2,4-dimethylpentan-3-one. The conversion to (**1d**) in preference to the formation of (**3d**) may be ascribed to the methyl group stabilising a radical or an enol arising from the C(1)–C(2) bond fission. It is known that benzocyclobutenols revert to the starting ketones on heating.<sup>5</sup> The IR spectrum of the benzocyclobutenone (**3d**) showed a four-membered carbonyl band at 1775 cm<sup>-1</sup>, and the <sup>1</sup>H NMR spectrum showed a doublet at  $\delta$  1.46 due to a methyl group and a quartet at  $\delta$  4.28 due to a C(2) methine proton. The photocyclization of *o*-alkylphenyl 1,3-diketones followed by thermal retro-aldol cleavage of the resulting benzocyclobutenols should prove useful for the preparation of benzocyclobutenones.

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<sup>‡</sup> Irradiation of (**1a**) in methanol gave 3-hydroxy-3-isopropyl-2,2-dimethyl-3,4-dihydronaphthalen-1(2*H*)-one in 56% yield.<sup>7</sup>