

PHOTOCHEMICAL DE-t-BUTYLATION OF 3,5-DI-t-BUTYL-4-HYDROXYPHENYL KETONES<sup>1</sup>

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Recently studies concerning the photochemical reactivity of aromatic ketones and their ring substituted derivatives have drawn much attention.<sup>2</sup> Porter and Suppan<sup>3</sup> reported that the photochemical disappearance of *p*-hydroxybenzophenone is very low ( $\phi = 0.02$ ) in isopropyl alcohol while it shows high reactivity ( $\phi = 0.9$ ) in cyclohexane leading to a corresponding pinacol. They suggested that the lowest lying excited state of *p*-hydroxybenzophenone may be a charge-transfer triplet in isopropyl alcohol and an  $n, \pi^*$  triplet in cyclohexane. We report that irradiation of 3,5-di-*t*-butyl-4-hydroxyphenyl ketones of type I in cyclohexane does not lead to pinacol formation via the  $n, \pi^*$  triplet but a novel de-*t*-butylation.

In accordance with the results reported by Porter and Suppan,<sup>3</sup> both Ia and Ib were unreactive on irradiation<sup>4</sup> in isopropyl alcohol and were recovered quantitatively. On irradiation in cyclohexane, however, 3,5-di-*t*-butyl-4-hydroxyacetophenone (Ia)<sup>5</sup> gradually reacted to give a crystalline hydroxy-ketone (IIa, > 95% based on the reacted Ia), m.p. 175-176°, which was also obtained in 60% yield by irradiation with a low-pressure mercury lamp (essentially 2537 Å light) in the same solvent. Treatment of this product with aluminum chloride in benzene yielded *p*-hydroxyacetophenone. The n.m.r. spectrum (60 Mc.) shows signals at  $\tau$  2.0-3.4 (3H, multiplet, aromatic protons), 7.48 (3H, singlet, -COMe), and 8.61 (9H, singlet, -CMe<sub>3</sub>). The structure IIa assigned was confirmed by a synthesis. Irradiation (2537 Å)<sup>6</sup> of *o*-*t*-butylphenyl acetate (IIIa) afforded IIa (24%) as crystals and IVa (26%) as an oil.

Irradiation of 3,5-di-*t*-butyl-4-hydroxybenzophenone (Ib)<sup>7</sup> under similar conditions also resulted in de-*t*-butylation to give 3-*t*-butyl-4-hydroxybenzophenone (IIb, > 95% based on the reacted Ib), the structure of which was confirmed by a synthesis. Irradiation (2537 Å) of *o*-*t*-butylphenyl benzoate (IIIb) afforded IIb (20%) as crystals, m.p. 179-180°, and IVb (35%) as an oil.

