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PHOTOCHEMICAL DE-t-BUTYLATION OF 3,5-DI-t-BUTYL-4-HYDROXYPHEWYL KETONES¹ Teruo Matsuura and Yoshihiko Kitaura

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Recently studies concerning the photochemical reactivity of aromatic ketones and their ring substituted derivatives have drawn much attention.² Porter and Suppan³ reported that the photochemical disappearance of p-hydroxybensophenone is very low ($\emptyset = 0.02$) in isopropyl alcohol while it shows high reactivity ($\emptyset = 0.9$) in cyclohexane leading to a corresponding pinacol. They suggested that the lowest lying excited state of p-hydroxybensophenone may be a charge-transfer triplet in isopropyl alcohol and an n, π^* 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 <u>via</u> the n, π^* triplet but a novel de-t-butylation.

In accordance with the results reported by Porter and Suppan,³ both Ia and Ib were unreactive on irradiation⁴ in isopropyl alcohol and were recovered quantitatively. On irradiation in cyclohexane, however, 3,5-di-t-butyl-4-hydroxyacetophenone (Ia)⁵ 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 bensene yielded p-hydroxyacetophenone. The n.m.r. spectrum (60 Mc.) shows signals at 7 2.0-3.4 (3H, multiplet, aromatic protons), 7.48 (3H, singlet, -COMe), and 8.61 (9H, singlet, -CMe₃). The structure IIa assigned was confirmed by a synthesis. Irradiation (2537 Å)⁶ of or -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)⁷ 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 <u>o</u>-t-butylphenyl benzoate (IIIb) afforded IIb (20%) as crystals, m.p. 179-180°, and IVb (35%) as an oil. Irradiation of the methyl ether of Ib in either a polar or nonpolar solvent resulted in pinacolization (55% in isopropyl alcohol and 30% in cyclohexane). The pinacol, m.p. $70-75^{\circ}$, was found to be a mixture of dl- and meso-forms (V) by n.m.r. analysis. The methyl ether of Ia was recovered quantitatively by irradiation in cyclohexane, while it gave three unidentified photo-products in isopropyl alcohol. The above results indicate that the presence of a free phenolic group in I is prerequisite to the photochemical de-t-butylation. It is assumed that the reactive species for the de-t-butylation of these p-hydroxyphenyl ketones bearing a hindered phenolic hydroxyl is not an $n_{s}x^{*}$ triplet state, but photoenolization may be involved. The scope and mechanistic studies of the present reaction are in progress. Satisfactory analyses were obtained for all new compounds.



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- (3) G. Porter and P. Suppan, <u>Proc. Chem. Soc.</u>, 191 (1961); <u>Trans. Faraday Soc.</u>, <u>61</u>, 1664 (1965).
- (4) Irradiations were made with a 450 w. high-pressure mercury lamp (Pyrex filter) under bubbling nitrogen, unless otherwise indicated.
- (5) T. Matsuura, A. Nishinaga, and H. J. Cahnmann, J. Org. Chem., 27, 3620 (1962).
- (6) Cf. H. Kobsa, <u>ibid.</u>, <u>27</u>, 2293 (1962).
- (7) C. D. Cook and N. D. Gilmour, *ibid.*, 25, 1429 (1960).

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