Photochemically Induced Reaction between a t-Butyl Side-chain and an *ortho*-Nitro-group

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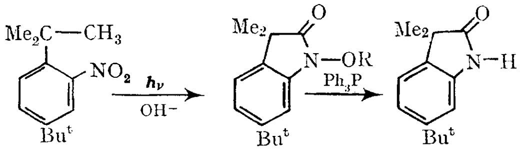
THE photochemistry of *o*-nitrobenzyl compounds involving attack at the α-carbon atom has been investigated recently.[1] Here a photochemical attack at the β-carbon atom of the side-chain is reported.

Irradiation of a 2% solution of 1-nitro-2,5-di-t-butylbenzene (I) in methanol containing sodium hydroxide (0·2M) with a high-pressure mercury arc through a Pyrex filter (3 hr., 12% conversion) followed by alkali extraction of the mixture gives 1-*N*-hydroxy-3,3-dimethyl-6-t-butylindol-2(3*H*)-one (IIa) (34%), m.p. 176—177°. If the irradiation is carried out without addition of alkali, the yield drops to 13%. When (I) is refluxed in methanolic sodium hydroxide solution for 24 hr. in the dark, < 0·02% of (IIa) is detected by u.v. analysis.

Structure (IIa) is confirmed† by a broad concentration-independent OH-absorption from 3500 to 2500 cm.$^{-1}$, ν(C=O) at 1692 cm.$^{-1}$; n.m.r. signals at τ −0·3 Br(1H), 3·20 (1H), 3·34 (2H), two singlets at 8·72 and 8·75 (together 15H); *m/e* 233 (M^+), 217 (M − O, m^* 205), 190 (M − HCNO, m^* 155; 217 − HCN, m^* 166). Addition of ferric chloride to a solution of (IIa) in ethanol produces an intense blue colour[2] which changes into purple upon addition of water and fades completely upon addition of either acid or alkali.



(I)

(II)a, R=H
b, R=Ac
c, R=Me

(III)

The acetate (IIb) [from (IIa) with acetic anhydride–pyridine], m.p. 122°, has ν(C=O) at 1809 and 1728 cm.$^{-1}$, n.m.r. signals at τ 3·31 (2H), 3·64 (1H), 7·77 (3H), 8·65 (6H, *gem*-Me), and 8·77 (9H, Bu^t); *m/e* 275 (M^+), 233 (M − CH$_2$CO, m^* 197·5), 217, and 190 (233 − HNCO, m^* 155). Methylation of (IIa) with diazomethane proceeds slowly to give (IIc), m.p. 86°, showing *m/e* 247 (M^+). Deoxygenation of (IIa) with triphenylphosphine gives triphenylphosphine oxide and a compound of m.p. 192°, ν(N–H) 3450 cm.$^{-1}$, ν(C=O) 1715 cm.$^{-1}$; τ 0·18 (1H), 2·95 (m, 3H), 8·60 (s, 6H), 8·68 (s, 9H); *m/e* 217 (M), 202 (M − 15, m^* 188), 174 (202 − CO, m^* 150), to which the γ-lactam structure (III) is assigned. Furthermore, the u.v. spectrum of (III) is in accord with that[3] of a series of methylated oxindoles.

The neutral fraction of the photolysis mixture consists mainly of starting material and at least seven minor components, which so far have not been characterized.

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† All compounds gave satisfactory elemental analyses. I.r. spectra were taken in CCl$_4$ or CHCl$_3$; n.m.r. spectra in CDCl$_3$. A cold inlet system was used with an Atlas CH 4 mass spectrometer.

[1] J. A. Barltrop and N. J. Bunce, *J. Chem. Soc.* (*C*), 1968, 1467; H. Morrison and B. H. Migdalof, *J. Org. Chem.*, 1965, **30**, 3996; G. Wettermark, *J. Amer. Chem. Soc.*, 1962, **84**, 3658.

[2] Note the similar reaction of an α-arylamino-nitrone with ferric chloride: H. G. Aurich, *Chem. Ber.*, 1965, **98**, 3917.

[3] Mme. Ramart-Lucas and Mlle. Biquard, *Bull. Soc. chim. France*, 1935, **2**, 1383.