Photolysis of *p*-Nitroacetophenone. An Unusual Formation of an Azoxybenzene

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Summary Photolysis of *p*-nitroacetophenone in propan-2-ol produced 4,4′-diacetylazoxybenzene as the major product.

In spite of considerable interest in the photochemical reduction of *para*-substituted aceto- and benzophenones,[1] no significant photoreduction has been reported for *p*-nitroacetophenone (1).[2,3]

p-$NO_2 \cdot C_6H_4 \cdot CX \cdot Me$
(1) X = O
(3) X = $-O \cdot (CH_2)_2 \cdot O-$

p-$Me \cdot CX \cdot C_6H_4 \cdot NY:N \cdot C_6H_4 \cdot CX \cdot Me$-*p*
(2) Y = X = O
(4) Y = nothing, X = $-O \cdot (CH_2)_2 \cdot O-$
(5) Y = nothing, X = O

Photolysis of (1) in propan-2-ol (12 h with a Hanovia 450-W lamp, Kimax-filtered) gave the diacetylazoxybenzene (2) (31%), m.p. 192°. Assignment of structure (2) to the product was made on the basis of its unusual mass spectrum[4] [*m/e* 282 (M^+, 75%), 267 (M–CH_3, 8%), 266 (M–O, 14%), 119 (M–NN(O)–$C_6H_4COCH_3$, 100%), 91 (M–NN(O)$C_6H_4COCH_3$–CO, 92%) and 43 (CH_3CO, 92%)] and its i.r., n.m.r., and u.v. spectra.

This structural assignment was supported by an unambiguous synthesis of (2). Thus, borohydride reduction in Me_2SO[5] of the ketal (3) [formed from (1)] gave the azo-compound (4) (85%), m.p. 170—171°. Acid hydrolysis of this produced the azobenzene (5), m.p. 217—218°, which upon oxidation with peracetic acid[6] gave (2); the latter was converted into the former by hydrogenation over 10% Pd-C.

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