

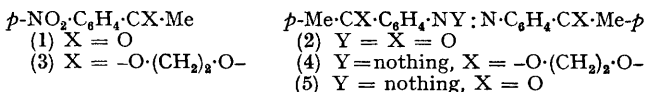
## Photolysis of *p*-Nitroacetophenone. An Unusual Formation of an Azoxybenzene

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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,<sup>1</sup> no significant photoreduction has been reported for *p*-nitroacetophenone (1).<sup>2,3</sup>



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<sup>4</sup> [ $m/e$  282 ( $M^+$ , 75%), 267 ( $M-\text{CH}_3$ , 8%), 266 ( $M-\text{O}$ , 14%), 119 ( $M-\text{NN}(\text{O})-\text{C}_6\text{H}_4\text{COCH}_3$ , 100%), 91 ( $M-\text{NN}(\text{O})\text{C}_6\text{H}_4\text{COCH}_3-\text{CO}$ , 92%) and 43 ( $\text{CH}_3\text{CO}$ , 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  $\text{Me}_2\text{SO}$ <sup>5</sup> 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<sup>6</sup> gave (2); the latter was converted into the former by hydrogenation over 10% Pd-C.

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<sup>5</sup> R. O. Hutchins, D. W. Lamson, L. Rua, C. Milewski, and B. Maryanoff, *J. Org. Chem.*, 1971, **36**, 803.

<sup>6</sup> B. T. Newbold, *J. Org. Chem.*, 1962, **27**, 3919.