

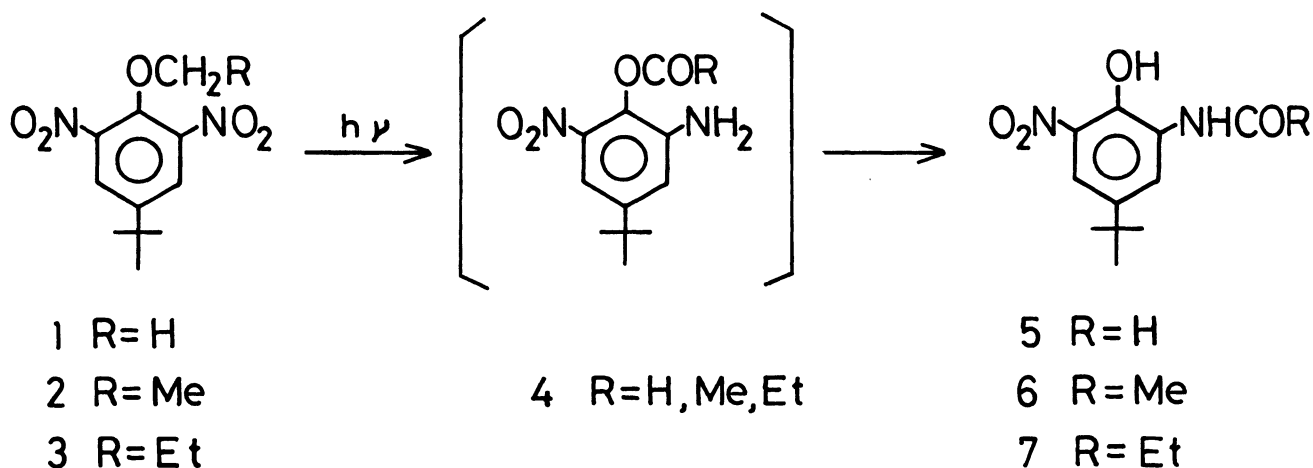
THE FORMATION OF 2-ACYLAMINO-4-t-BUTYL-6-NITROPHENOLS BY THE PHOTO-IRRADIATION OF 1-ALKOXY-4-t-BUTYL-2,6-DINITROBENZENES

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The photo-irradiation of 1-methoxy-, 1-ethoxy-, and 1-n-propoxy-4-t-butyl-2,6-dinitrobenzenes gave 2-formylamino-, 2-acetylamino-, and 2-propanoylamino-4-t-butyl-6-nitrophenols, respectively. The structures of these photo-irradiation products were confirmed by the comparison with the synthetic samples.

In the course of the studies on the photo-irradiation of 1-methoxy-, 1-ethoxy-, and 1-n-propoxy-4-t-butyl-2,6-dinitrobenzenes (1, 2, and 3), the novel herbicides,<sup>1)</sup> we found the formation of 2-formylamino-, 2-acetylamino-, and 2-propanoylamino-4-t-butyl-6-nitrophenols (5, 6, and 7), respectively. Although many reports on the photochemistry of nitro compounds have appeared,<sup>2)</sup> the photo-reaction of such 1-alkoxy-2,6-dinitrobenzenes has not been reported yet.



The dinitro compounds, 1 (mp 102-103 °C), 2 (mp 96-97 °C), and 3 (mp 108-109 °C), were prepared by the nitration of the corresponding t-butylphenyl ethers.

A solution of 1 (2.0 g) in 500 ml of dry benzene was irradiated by a high-pressure 450 W mercury arc for 30 h under a nitrogen atmosphere at room temperature. After irradiation, the solvent was removed in vacuo and the residue was chromatographed on silica gel by elution with benzene-ethyl acetate (1:1) to afford crude 5, which was further chromatographed with carbon tetrachloride-ethyl acetate-acetic acid (60:20:1.5) to give 5 (45 mg, 14.1%<sup>3)</sup>): mp 131-132 °C (from methanol), IR (KBr) 3250 (OH), 1660 (C=O), and 1540 cm<sup>-1</sup> (NO<sub>2</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.28 (9H, s, t-Bu), 7.78 (1H, d, J=2.2Hz, 3-H), 7.86 (1H, br.s, OH), 8.51 (1H, s, CHO), 8.82 (1H, d, J=2.2Hz, 5-H), 10.92 (1H, s, NH); MS m/e (rel intensity), 238 (15, M<sup>+</sup>), 223 (100), and 195 (100).

Similarly, 6, mp 146-147 °C (12.6%<sup>3)</sup>) and 7, mp 122-123 °C (28.2%<sup>3)</sup>) were obtained by a manner similar to that of 5, respectively.<sup>4)</sup>

These photo-irradiation products (5, 6, and 7) were identical in all respects with the authentic samples obtained by the nitration of the corresponding 2-acylamino-4-t-butylphenols.<sup>5)</sup>

The mechanisms of these photo-reaction are not clear since no intermediates have been isolated. Although the formation of some intermediates would be expected, it is assumed that the formation of 5, 6, and 7 can arise from the migration of acyl groups of the intermediate 4, which is produced by the intramolecular one-sided oxidation-reduction between the alkoxy and nitro groups of 1, 2, and 3. Further examination of the minor photo-irradiation products is now in progress.

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#### References

- 1) S. Nagato, N. Takagi, and H. Obara, Japan Tokkyo Kokai, 56-2901 (1981).
- 2) H. A. Morrison, "The Chemistry of the Nitro and Nitroso Groups", ed by H. Feuer, John Wiley & Sons (1969), Part I, p. 165.
- 3) This yield is based on the consumed starting materials.
- 4) The IR and MS spectra of these compounds were as follows.  
Compound 6: IR (KBr) 3280 (OH), 1672 (C=O), and 1545 cm<sup>-1</sup> (NO<sub>2</sub>); MS m/e (rel intensity), 252 (36, M<sup>+</sup>), 210 (84), and 195 (100).  
Compound 7: IR (KBr) 3280 (OH), 1690 (C=O), and 1542 cm<sup>-1</sup> (NO<sub>2</sub>); MS m/e (rel intensity), 266 (29, M<sup>+</sup>), 210 (100), and 195 (56).
- 5) The details of these synthetic procedures will be reported elsewhere.

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