# Quantitative Photodecarbonylation of Formanilides: a New Photosensitive Protecting Group for Anilines

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*Summary* Since irradiation of formanilides causes quantitative decarbonylation, formanilides are suggested as a new photosensitive protecting group for anilines.

LITTLE has been published on photosensitive protecting groups for amines.[1] Irradiation of either *o*-nitrobenzyl or benzyloxycarbonyl derivatives of amino-acids produces high yields of the free amino-acid.[1b,c] Irradiation of formates yields phenols in moderate yields.[1d] These results suggest formamides as possible photosensitive protecting groups for amines. However, previous work on the photochemistry of formamide does not mention decarbonylation,[2] and instead adducts result in low yields in the presence of olefins, acetylenes, and aromatic compounds. Yields are increased in the presence of acetone, which may serve as an initiator rather than a sensitizer.[2b] At low temperatures irradiation of formamide forms radicals.[2c] For formanilides, it is possible that photolysis will cause photo-Fries type rearrangement.[2d] Previous results thus mask the possibility that formamides may undergo photodecarbonylation. We report here results of such irradiations which show that formanilides may be useful photosensitive protecting groups for anilines.

Three formanilides were prepared by mixing a solution of the corresponding commercially available aniline in ether with 98% formic acid and keeping the mixture at 0 °C for 3 days.[3] Work-up of the precipitate afforded the respective formanilides: formanilide, m.p. 47·5°,[4] *m/e* 121 ($M^+$ 100), 93 (100), and 66 (85); *m*-trifluoromethylformanilide, m.p. 50—53°,[5] *m/e* 189 ($M^+$ 10), 170 (34), 160 (61), 113 (100), 110 (80), 64 (47), and 62 (68); 3,4,5-trimethoxyformanilide, m.p. 68—70°, *m/e* 211 ($M^+$ 46), 196 (73), 167 (43), 139 (100), 124 (35), 109 (84), and 67 (46). In contrast to photolysis (see later) ionization in the mass spectrometer does not always lead to decarbonylation.

Upon irradiation (254 nm) of each formanilide (*ca.* 0·1 g) in MeCN (*ca.* 1 ml) under $N_2$ in quartz n.m.r. tubes, gas bubbles formed and the pressure in the tube increased; the reaction was monitored by n.m.r. spectroscopy. The absorption of the starting formanilide decreased in intensity as peaks due to the product aniline appeared and increased in intensity. Upon work-up only aniline (*ca.* 100%) could be isolated. Rates of disappearance of amide were approximately the same for each amide. Irradiation of formamide in trideuterioacetonitrile did not result in deuterium incorporation into aniline.

In a separate experiment the same three formanilides were dissolved in diphenyl ether and heated at 220° for over 100 h. Although the $^1H$ n.m.r. spectrum was scanned repeatedly, no change was noted. Thus one should be able to convert anilines, and perhaps alkylamines,† into formamides, carry out a wide variety of transformations,‡ and then regenerate the beginning amine by irradiation and loss of carbon monoxide.

Acknowledgement is made to the Atomic Energy Commission for partial support, and to the National Science Foundation for Research Instruments Grants.

(*Received, 27th March* 1972; *Com.* 501.)

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† Work is in progress on a wide range of formamides.

‡ Pyrex glass vessels will shield from decomposition those amides that do not absorb light above 300 nm. Others must be allowed to react in the dark.

[1] (a) For a recent survey on photosensitive protection groups see: P. G. Sammes, *Quart. Rev.*, 1970, **24**, 37; (b) J. A. Baltrop and P. Schofield, *J. Chem. Soc.*, 1965, 4758; (c) C. A. Patchornik, B. Amit, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1970, **92**, 6333; (d) W. M. Horspool and P. L. Pauson, *J. Chem. Soc.*, 1965, 5162.

[2] (a) D. Elad in 'Organic Photochemistry,' ed. O. L. Chapman, Marcel Dekker, New York, 1969, vol. II, pp. 196—200; (b) J. Ollivier and C. Leibovici, *Tetrahedron*, 1971, **27**, 5515; (c) R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1967, **47**, 4173; S. R. Bosco, A. Cirillo, and R. B. Timmons, *J. Amer. Chem. Soc.*, 1969, **91**, 3140; (d) V. I. Stenberg in 'Organic Photochemistry,' ed., O. L. Chapman, Marcel Dekker, New York, 1967, vol. I, pp. 127ff.

[3] Modification of the method of R. Camps, *Ber.*, 1901, **34**, 2703.

[4] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, 'The Systematic Identification of Organic Compounds,' 4th edn., Wiley, New York, 1948, p. 285.

[5] G. R. Pettit, M. V. Kalmins, T. M. H. Lin, E. G. Thomas, and K. Parent, *J. Org. Chem.*, 1961, **26**, 2563.