Competitive Photo-ethoxylation and -hydroxyethylation of Pyridine-2-carbonitrile in Acidic Ethanolic Solutions

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Summary U.v. irradiation of pyridine-2-carbonitrile (**1**) in acidic ethanolic solution gives 6-ethoxypyridine-2-carbonitrile (**2**) and 2-(1-hydroxyethyl)pyridine (**3**); (**2**) is formed *via* an excimer and (**3**) by a radical mechanism.

WE have already reported the photochemical alkoxylation of pyridine-2-carboxylic acid and methyl pyridine-2-carboxylate and proposed a mechanism *via* an excimer. We now report competition between ethoxylation and hydroxyethylation in the u.v. irradiation of pyridine-2-carbonitrile (**1**) in acidic ethanolic solutions.

A solution of (**1**) in ethanol containing $0{\cdot}05$ mol/dm^3 excess of H_2SO_4 was irradiated with a low-pressure mercury lamp (17 W) under nitrogen. Two photoproducts (**2**) and (**3**) were formed.†

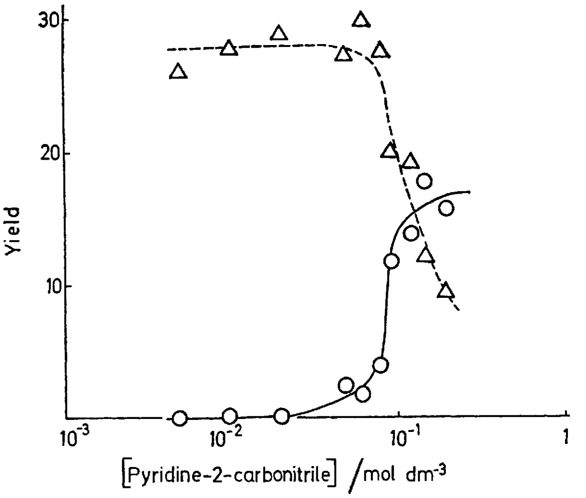
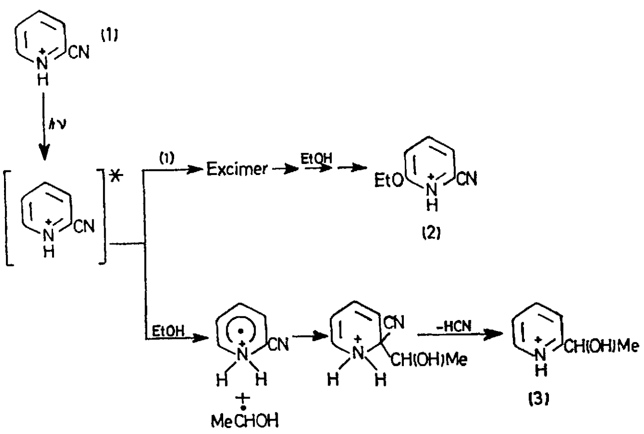


FIGURE. Concentration dependence of the photo-reaction; ——○—— yield of (**2**), --- △ ---yield of (**3**). Yield = 100 × [amount of product]/[amount of (**1**) consumed].

The yields of the photoproducts are plotted against the concentration of (**1**) in the Figure. Photo-ethoxylation and -hydroxyethylation are competitive, hydroxyethylation being dominant at low concentrations of (**1**). The photo-ethoxylation of (**1**) has the same concentration dependence as that of pyridine-2-carboxylic acid and methyl pyridine-2-carboxylate. Kinetic treatment indicated excimer participation for the latter,[2] so we suggest that (**2**) is probably formed *via* an excimer.

A radical mechanism has been suggested for the photo-substitution of CN by hydroxyalkyl groups in alcoholic solutions for quinoline-2-carbonitrile.[3] The photo-hydroxyethylation of (**1**) thus probably proceeds by a similar radical mechanism.



SCHEME

Photo-ethoxylation and -hydroxyethylation occur more effectively in the presence of mineral acid than in its absence. The photoreactions of pyridine-2-carbonitrile are summarized in the Scheme.

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† Products were identified by elemental analyses and spectral data. Reaction mixtures were analysed quantitatively by g.l.c.

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[3] N. Hata, I. Ono, S. Matano, and H. Hirose, *Bull. Chem. Soc. Japan*, 1973, **46**, 942; N. Hata and T. Saito, *ibid.*, 1974, **47**, 942.