

PHOTOREACTIONS OF HETEROAROMATIC COMPOUNDS III* PHOTO-HYDROXYLATION AND
ALKOXYLATION OF 2-PYRIDINECARBOXYLIC ACID IN ACIDIC AQUEOUS AND ALCOHOL
SOLUTIONS

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Previously we reported that 3-pyridinecarboxylic acid shows manifold photoreactivities depending on the solvent and the acidity of the media.¹⁾ 3-Pyridinecarboxylic acid undergoes photo-hydroxylation in acidic aqueous solution and photo-ethylation in acidic ethanol solution. In this paper, we report the photochemical hydroxylation and alkoxylation of 2-pyridinecarboxylic acid in acidic media.

The solution of 2-pyridinecarboxylic acid in aqueous and alcohol solutions, the acidity of which was adjusted with sulfuric or hydrochloric acid, was irradiated with a low pressure mercury lamp under nitrogen or air.

In acidic aqueous solution, 2-pyridinecarboxylic acid gave 6-hydroxy-2-pyridinecarboxylic acid in 30 % yield. Photo-hydroxylation is a common photoreaction among 2- and 3-pyridinecarboxylic acid and their derivatives such as ester, amide and nitrile. In Fig.1 are shown the relations of photo-reactivity as well as the molar extinction coefficient at 264 nm of 2-pyridinecarboxylic acid to the acidity of the solution. Both curves show increase at the acidity where pyridinium salt begins to form. Photo-hydroxyl-

ation was quenched by oxygen. This suggests that the reaction proceeds via a triplet state. The acidity dependence of the photoreaction can be reasonably interpreted by the intermediacy of triplet state. It is known that pK_a values of the triplet state of pyridine derivatives are similar to those of the ground state, whereas pK_a 's of the excited singlet state are greatly different.²⁾

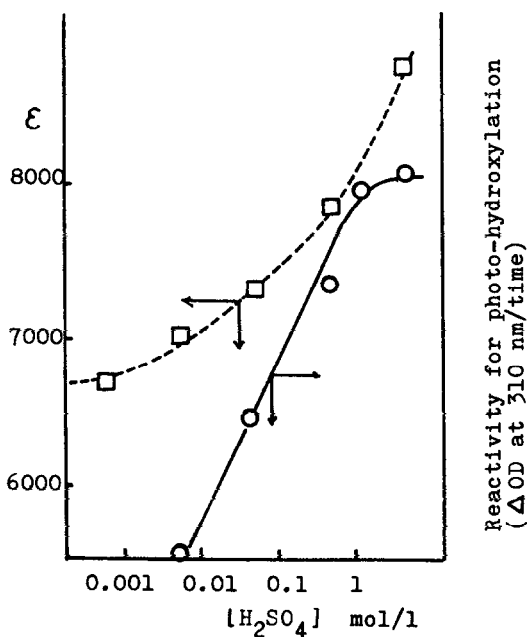
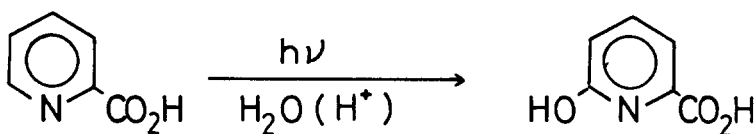


Fig.1 Relation of reactivity for photo-hydroxylation($\text{---}\circ\text{---}$) and molar extinction coefficient at 264 nm($\text{---}\square\text{---}$) of 2-pyridinecarboxylic acid to the acidity of the solution

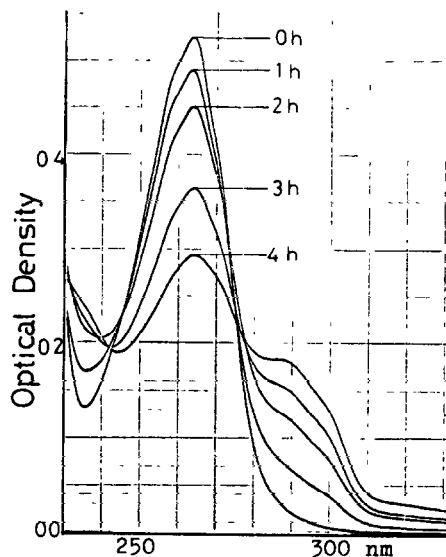
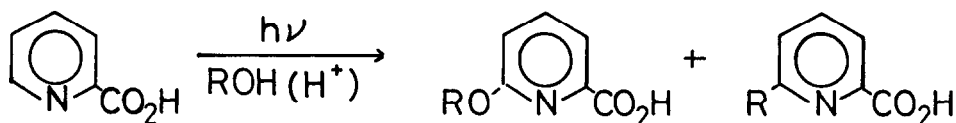


Fig.2 UV-spectral change of 2-pyridinecarboxylic acid (0.005 mol/l) in acidic ethanol solution ($[\text{H}_2\text{SO}_4]=0.5$ mol/l) during UV-irradiation

An important difference in the photoreactivities between 2- and 3-pyridine-carboxylic acid was observed in the photoreaction in acidic alcohols. The UV-spectral change during irradiation was shown in Fig.2. As was reported previously,¹⁾ 3-pyridinecarboxylic acid gave photochemically 4-ethyl-3-pyridine-carboxylic acid in acidic ethanol solution. Photo-alkylation in alcohol solutions is one of the photoreactions characteristic of N-heteroaromatic compounds.³⁾ 2-Pyridinecarboxylic acid, on the other hand, undergoes photo-alkoxylation in acidic alcohol solutions. During UV-irradiation in acidic ethanol solution, 2-pyridinecarboxylic acid gave mainly 6-ethoxy-2-pyridine-carboxylic acid, the structure of which was determined by elementary analysis (Found: C, 58.02 % ; H, 5.54 %; N, 8.14 %, Calcd. for $C_8H_9NO_3$: C, 57.48 %, H, 5.39 %, N, 8.38 %) and by comparison of the UV-, IR- and NMR-spectra with those of 6-hydroxy-2-pyridinecarboxylic acid. Photoethylation was, in this case, a minor reaction, occurring at a ratio of one to five with respect to photo-ethoxylation.

Photo-alkoxylation was observed in acidic methanol solution, but not in acidic 2-propanol solution. In contrast to the general tendency of N-heteroaromatic compounds to undergo photo-alkylation in radical mechanism, 2-pyridine-carboxylic acid undergoes photo-alkoxylation, which is considered to be an ionic reaction.



R=Me, Et

Photo-alkoxylation could be regarded as the same type of reaction as photo-hydroxylation in acidic aqueous solution. However, photo-alkoxylation differs from photo-hydroxylation in that the former is dependent on the concentration of 2-pyridinecarboxylic acid and occurred only at the higher concentration of the substrate (Fig.3), while the latter occurred even at the lower concentration of 2-pyridinecarboxylic acid. This suggests that the photo-alkoxylation proceeds via a sort of complex (presumably a excimer). In parallel with photo-hydroxylation, photo-alkoxylation was quenched by oxygen and occurred in solutions

where the concentration of sulfuric acid is above $\sim 10^{-2}$ mol/l. At this acidity, 2-pyridinecarboxylic acid is converted to the pyridinium form. This indicates that the photo-alkoxylation is initiated by the excitation of 2-pyridinecarboxylic acid in pyridinium form.

The photochemical addition of water and alcohols

to phenazine studied by Inoue et al.⁴⁾ would be a reaction similar to this photo-substitution. However, in the reaction of phenazine, the process of the hydrogen elimination does not occur.

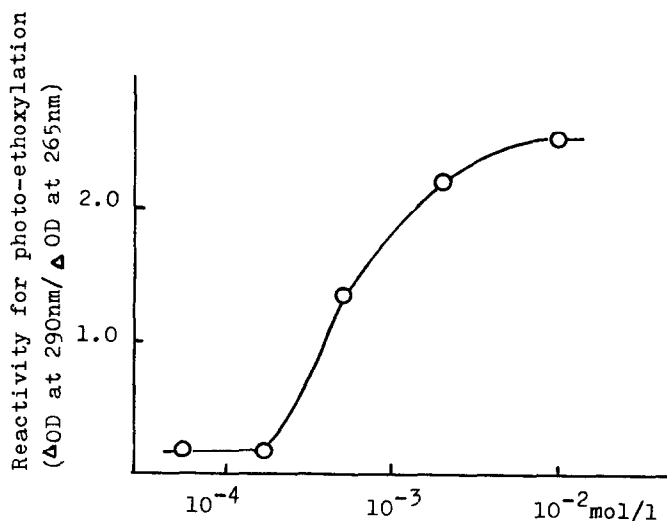


Fig.3 Dependence of photo-ethoxylation on the concentration of 2-pyridinecarboxylic acid

- *) Part I. C. Azuma and A. Sugimori, Kogyo Kagaku Zasshi, 72, 239 (1969)
 Part II. F. Takeuchi, T. Fujimori and A. Sugimori, Bull. Chem. Soc. Jap., 43, 3637 (1970)
- 1) Part II of the series
 - 2) G. Jackson and G. Porter, Proc. Roy. Soc., A260, 13 (1961)
 - 3) References are cited in 1)
 - 4) H. Inoue, T. Ochiai, A. Sugimoto and E. Imoto, Bull. Chem. Soc. Jap., 44, 3101 (1971)