PHOTO- AND RADIATION-INDUCED ALKYLATION, HYDROXYALKYLATION, AND ALKOXYLATION OF PYRIDINECARBOXAMIDES IN ALCOHOL

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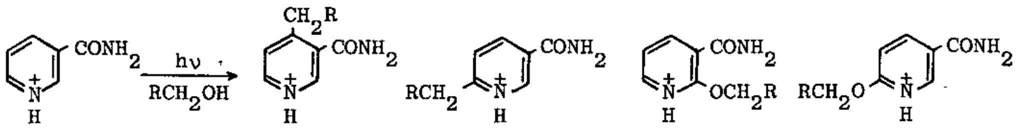
The UV-irradiation of pyridinecarboxamides in alcohol brings about alkoxylation (ionic reaction) and/or alkylation and hydroxyalkylation (radical reactions). The types of photoreaction and the position at which reaction occurs depend on the structure of the substrates, the acidity of the solutions, and the additives.

2-Pyridinecarboxamide(**1**) is alkylated at the 5-position in the absence of added acid via the hydrogen abstraction by the excited ester carbonyl and at the 4-position in the presence of H_2SO_4 via the hydrogen abstraction by the protonated N atom of the excited **1** . The UV-irradiation of 3-pyridinecarboxamide(**2**) in acidic alcohol brings about both alkylation and alkoxylation in parallel.



The effects of additives (triplet quenchers and electron acceptors) indicate that the two alkylation reactions originate from a common triplet state and the alkoxylation reactions at the 2- and 6-position originate from different excited singlet states. The photoreaction of **2** is characterized by the simultaneous participation of the various kinds of excited states. 4-Pyridinecarboxamide(**3**) gives photochemically 2-(1-hydroxyalkyl)-4-pyridinecarboxamide regardless of the presence of added acid.

Gamma -irradiation of pyridinecarboxamides in acidic alcohol brings about alkylation and hydroxyalkylation in high efficiencies. This reaction is useful for the introduction of alkyl group to pyridine ring. The radiation-induced alkylation and hydroxyalkylation are similar to the radical type reactions induced by UV-irradiation.