PHOTOCHEMICAL ADDITION OF ACRYLONITRILE TO IMIDAZOLES AND INDOLES

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On irradiation in the presence of acrylonitrile in either a protic or an aprotic polar solvent, indoles gave their α-cyanoethyl derivatives. The cyanoethylation occurred at 1-, 2-, 3- or 4-position depending upon the substituent of the starting indoles and upon the solvent employed. For example, indole gave 3-(α-cyanoethyl)indole in both methanol and acetonitrile, and 3-methylindole gave 1-(α-cyanoethyl)indole inacetonitrile while it gave 2- and 4-(α-cyanoethyl)indoles in methanol. For this photo-cyanoethylation, a mechanism involving exciplex formation is proposed on the basis of the quenching of indole fluorescence with acrylonitrile.

The photoreaction of imidazoles in the presence of acrylonitrile was more complex. Irradiation of N-unsubstituted imidazoles in the presence of acrylonitrile gave α-cyanoethyl derivatives in either ethanol or acetonitrile. Thus, 2-phenylimidazole gave 2-phenyl-4-(α-cyanoethyl)imidazole and 2-phenyl-2-(α-cyanoethyl)imidazole, and 2,4,5-triphenylimidazole (lophine) gave 2-phenyl-2-(α-cyanoethyl)imidazole. The main product from the photolysis of N-substituted imidazoles in the presence of acrylonitrile was found to be a [2 + 2] cycloadducts between C=C double bonds of the reactants in ethanol and to be a 5-imidazolone derivative in acetonitrile; for example, 1-methyl-2,4,4-triphenylimidazolone was obtained from N-methyllophine. The formation of the 5-imidazolone is rationalized in terms of the formation of a 1-azetine intermediate which is formed by [2 + 2] cycloaddition between the 4,5-double bond of imidazoles and the C≡N triple bond of acrylonitrile. A 1-azetine type cycloadduct was isolated from the photolysis products of N-methyllophine and 2-cyanopyridine.