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Photo-induced Isomerization of Aryl Isocyanides into Cyanides

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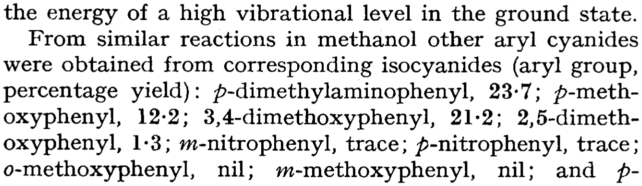
Summary The photo-induced isomerization of an aryl isocyanide in methanol into a cyanide received assistance from a strong electron donating substituent in the *para*-position; in aprotic solvents the rearrangement was inhibited.

THE first condensed phase photo-induced isomerization of an isocyanide into a cyanide has been achieved by irradiating solutions of certain aryl isocyanides. Previously methyl isocyanide was known to photo-isomerize into acetonitrile in the gas phase.[1]

A 7 mM solution of an aryl isocyanide in degassed methanol was irradiated at 254 nm for 90 h under nitrogen in a Rayonet Photochemical Reactor equipped with 16 low pressure mercury lamps. In the most efficient example 2,4-dimethoxyphenyl isocyanide (**1**) gave 2,4-dimethoxyphenyl cyanide (**2**) in 52·2% yield. The possibility of a thermal reaction was eliminated by heating the isocyanide (**1**) in methanol under reflux for 90 h. This did not produce a detectable amount of the cyanide (**2**) and permitted nearly quantitative recovery of (**1**).

When other solvents replaced methanol during irradiation, the yield of (**2**)—reduced to 12·5% in dichloromethane, to 7·1% in benzene, and to 6·0% in cyclohexane—revealed assistance from methanol, probably by hydrogen bonding. Hydrogen bonding to the isocyano-carbon has been described for isocyanides in alcohols[2] and extended to the methanol solution of an aryl isocyanide under irradiation.[3] An increase in electrophilicity at an isocyano-carbon undergoing hydrogen bonding would be expected to facilitate migration from nitrogen to carbon in an aryl isocyanide by either a σ or π route.[4] The beneficial effect of an electron donating group in the *para* position is reminiscent of the similar *para*-substituent effect on the stabilization of an intermediate phenonium ion[5] and gives a preference for rearrangement by the π route with a similar intermediate. Insofar as electron donation from a *para*-substituent may be ineffective in an excited state molecule,[6] the suggested resonance stabilized intermediate (A) is presumed to have the energy of a high vibrational level in the ground state.



From similar reactions in methanol other aryl cyanides were obtained from corresponding isocyanides (aryl group, percentage yield): *p*-dimethylaminophenyl, 23·7; *p*-methoxyphenyl, 12·2; 3,4-dimethoxyphenyl, 21·2; 2,5-dimethoxyphenyl, 1·3; *m*-nitrophenyl, trace; *p*-nitrophenyl, trace; *o*-methoxyphenyl, nil; *m*-methoxyphenyl, nil; and *p*-chlorophenyl, nil. The rearrangements which are measurable in methanol are either barely detectable or non-occurring in dichloromethane, cyclohexane, or benzene. Investigations are continuing.

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