1,3-DIPOLAR CYCLOADDITION REACTIONS OF BENZYLIDENE CYANOAMINES

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Intermolecular and intramolecular cycloaddition reactions of benzylidene cyanamoines via their 1,3-dipolar tautomers were investigated.

**Intermolecular Reaction.** Benzylidene cyanobenzylamine 3 reacted with dimethyl acetylenedicarboxylate to give the expected 1:1 adduct, 3-pyrroline, together with pyrrole derivative arising from a 1:1 adduct with elimination of hydrogen cyanide. The reaction of 3 with dimethyl fumarate gave a mixture of pyrrolidine (1:1 adduct) and 1-pyrroline derived from a 1:1 adduct with elimination of hydrogen cyanide, whereas 3 reacted with dimethyl maleate to give the same 1-pyrroline as the sole product. The stereochemical course of the above reactions is also discussed. On the other hand, it has been found that cycloaddition reaction competed with ene-reaction and Michael type addition reaction in the reaction with N-(p-nitrophenyl)maleimide; in contrast to the reaction in refluxing benzene, cycloaddition reaction proceeded preferentially in refluxing toluene to give two stereoisomeric 1-pyrrolines arising from a 1:1 adduct with elimination of hydrogen cyanide.

**Intramolecular Reaction.** Next, intramolecular cycloaddition reactions of benzylidene cyanobenzylamines, 15, 16, 18, 19, 20, having alkylnyl or alkenyl groups have been investigated. On heating in xylene, all the benzylidene cyanamoines afforded products derived from intramolecular cycloadducts with the elimination of hydrogen cyanide.