HETEROCYCLES, Vol. 21, No 2, 1984

Heterocyclic Synthesis via Cu(I)-promoted Arylation of Anionic Species

Hitomi Suzuki*, S. V. Thiruvikraman, and Atsuhiro Osuka
Department of Chemistry, Faculty of Science,
Ehime University, Bunkyo-cho 2-5, Matsuyama 790, Japan

Copper(I) iodide dissolves into hot hexamethylphosphoric triamide (HMPA) to yield a black solution, where a variety of nucleophiles including ArS^-, $ArSe^-$, $ArTe^-$, $C_6H_4(CO)_2N^-$, $(RO)_2P(O)^-$, Ph_2P^-, Ph_2As^-, and stable enolates can be smoothly arylated with nonactivated aryl halides. The reaction is remarkably insensitive to the steric effects of ortho substituents or the presence of free amino group in aryl halides. The reaction has been extended successfully to the synthesis of heterocyclic compounds by the use of o-iodoaniline (1) as the aryl halide. Synthesis of 2-phenylbenzothiazole was achieved by the reaction of (1) with copper(I) thiobenzoate in 92% yield. Similarly, the reaction of (1) with sodiodimedone gave a 65% yield of a carbazole derivative in one pot procedure.

Further, intramolecular cyclization of N-2-haloaryl- and N-(2-haloaryl)methyl-substituted enaminones were achieved by heating in the presence of CuI in HMPA to give the corresponding heterocyclic compounds in good yields.

A clearer understanding has evolved through our investigations of the versatility and scope of the reaction especially with a view to synthesize a number of novel heterocycles.