SYNTHESIS OF 3-ALKYL- AND 3-ARYLPYRIDINES

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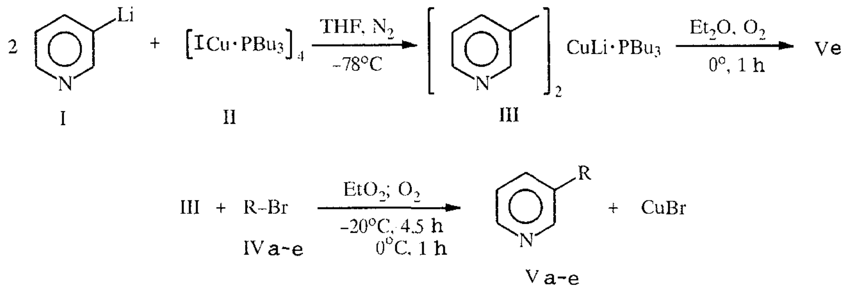
In our search for a convenient method for obtaining 3-n-butylpyridine — a specific toxic metabolite of fungi-inducers of *Fusarium* wilt of cotton, tomatoes, etc. [1] — we discovered a general method for obtaining 3-alkyl(aryl)pyridines using our complex of di(3-pyridyl)copperlithium with tri-n-butylphosphine (III).

Its reaction with alkyl and aryl bromides IVa-e in a ratio of 4:1 leads to 3-alkyl- and 3-arylpyridines Va-d in good yields (62-88%), while oxidation with oxygen immediately after their production leads to 3,3′-dipyridyl (Ve) in 65% yield.



IV, V a R = Et, b R = Bu, c R = Ph, d R = 2- pyridyl, e R = 3-pyridyl

The reaction of 3-pyridyllithium (I), obtained from 3-bromopyridine [31.6 g (0.2 lmole)] and butyllithium [2] with tetrakis[iodo(tributylphosphine)copper(I)] (II) [3] in THF at −78°C leads to complex III, the composition of which was established by the method in [4].

Compound III is only slightly soluble in THF; the solvent was removed by decantation, 100 ml of ether was added to the reaction flask, and, without raising the temperature above −20°C, a solution of 0.05 lmole of bromo derivative IV in 25 ml of ether was added in the course of 30 min. The mixture was then stirred for 4 h at −20°C. After this, dry oxygen was passed through the solution at 0°C for 1 h at a rate of 70-80 ml/min (oxidation of complex III prior to treatment of it by IV leads to Ve). The reaction mixture was decomposed with water, acidified with HCl solution to pH 5, and extracted with benzene to remove the tri-n-butylphosphine. The residue was made alkaline to pH 14 and steam distilled. The Va-e bases were extracted with ether and fractionally distilled in vacuo (20 mm). The yields were determined relative to IVa-e.

Compound Va. This compound was obtained in 88% yield and had bp 60-62°C and n_D^{20} 1.5010 (n_D^{20} 1.5002). The picrate had mp 128-130°C (from alcohol).

Compound Vb. This compound was obtained in 86% yield and had bp 98-100°C and n_D^{20} 1.4970 (n_D^{20} 1.4972 [5]). The picrate had mp 89°C (from alcohol) (mp 89-90° [5]).

Compound Vc. This compound was obtained in 77% yield and had bp 148-150°C and n_D^{20} 1.6167. The picrate had mp 159-160°C (n_D^{20} 1.6170, picrate mp 162°C [5]).

Compound Vd. This compound was obtained in 62% yield and had bp 170-172°C. The picrate had mp 153-154°C, 151-152°C (from alcohol) (n_D^{20} 1.6223, picrate mp 153-154°C [5]).

Compound Ve. This compound was obtained in 65% yield and had bp 171-174°C and mp 68°C. The picrate had mp 231-232°C (from water) (mp 232°C [5]).

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