STEREOSELECTIVE PREPARATION OF 2-ALKENYLPYRIDINES FROM α-SILYL CARBANION AND THEIR BIOLOGICAL ACTIVITIES

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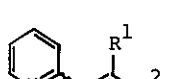
In the course of our investigation on a preparation of 2-alkenylpyridines **1** from α-silyl carbanion, we have reported that lithiated 2-(trimethylsilylmethyl)-pyridine **2** reacted with imines to give stereospecifically (E)-**1** in high yield. Furthermore, **2** reacted with benzaldehyde N-methylphenylhydrazone under reflux in the presence of crown ethers to give (E)-**1a** in high yield. In the presece of [2.1.1]-criptand, however, (Z)-**1a** was obtained at low temperature in low yield, while (E)-**1a** was a major product under reflux.

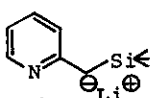
When boron trifluoride 1 : 1 adduct of benzaldehyde was added to **2** at low temperature, a mixture of (E)- and (Z)-**1a** was obtained in low yield (22%, E/Z = 78.9 : 21.1). However, addition of an excess amount of boron trifluoride (2 equivalents) increased the yield of **1a** (60%, E/Z = 85 : 15). In addition, the yield of **1a** was 51% when **2** was added to a solution of benzaldehyde-boron trifluoride 1 : 1 adduct at low temperature (E/Z = 87.1 : 12.9). On the other hand, benzaldehyde-titanium tetrachloride adduct gave only (E)-**1a**, but in low yield (30%).

^{7}Li-nmr of **2** in THF shows a sharp singlet, complicated with a broad signal, at δ -0.22, and that of a reaction mixture of **2** with benzilideneaniline shows a singlet at δ 0.0.

At last, pesticidal activities of **1a** - **1d** were evaluated. Each of these compounds shows a strong herbicidal and/or fungicidal activity (70 - 100% inhibition or disease control).



1 **a**, R^1 = H, R^2 = C_6H_5 **c**, R^1 = H, R^2 = 2-Py
b, R^1 = H, R^2 = C_6H_5CH=CH **d**, R^1 = R^2 = C_6H_5



2