Organosilicon Compounds. VIII.

Cleavage of the Silicon-Carbon Bond in 2-(Trimethylsilyl)pyridine with Benzaldehyde.

Frank II. Pinkerton and Shelby F. Thames

Department of Chemistry, University of Southern Mississippi

Sir:

Recently, Anderson (1-7), et al., have investigated the cleavage of 2-(trialkyl- and triarylsilyl)pyridines by water and alcohols and in a proposed mechanism stated the necessity of having both a nucleophilic center in the solvent molecule and also an electrophilic hydrogen for hydrogen bonding to the nitrogen of pyridine. These investigators noted that hydroxide ion had little effect on the rate of solvolysis and that methoxide ions were less reactive than methanol. These unexpected results prompted a statement that the solvolysis of 2-silyl substituted pyridines may require "a highly favourable special reaction path for neutral solvent molecules" (2).

Recent findings in these laboratories suggest that indeed 2-trimethylsilylpyridine provides for an unusually labile silicon-carbon bond that is cleaved readily by neutral reagents, in our hands benzaldehyde (Scheme A), giving rise to I in 89% yield.

This unusual silicon-carbon cleavage warrants further investigation to determine the scope and limitations of such a reaction. Investigations of this type are in progress on the pyridyl and similar aromatic systems.

The production of 1 was verified by complete elemental analysis, N.M.R. and infrared spectroscopy, as well as by the production of II, a known compound (8), from the ethanolysis of 1. The NMR is consistent with the structure of I as it exhibited a distorted doublet, representing the 6-pyridyl proton, at $1.64\,\tau$ and integrating for one proton, multiplets from 2.4 to $3.2\,\tau$ integrating for the remaining eight aromatic protons, a singlet at $4.1\,\tau$ integrating for one methine proton and a singlet at $9.93\,\tau$ integrating for nine protons of the trimethylsilyl group.

EXPERIMENTAL

The reaction of benzaldehyde (10.6 g., 0.1 mole) with 2-(trimethylsilyl)pyridine (15.1 g., 0.1 mole) at 100° for three hours afforded, after fractionation, 23.0 g. (89%) of 1, b.p. $86^{\circ}/0.03$ mm., $n_{\rm D}^{28}$ 1.5242.

Anal. Calcd. for C₁₅H₁₉NOSi: C, 69.98; H, 7.45; N, 5.44; Si, 10.91. Found: C, 70.25; H, 7.32; N, 5.62; Si, 10.70.

The refluxing of I (12.8 g., 0.05 mole) in 95% ethyl alcohol containing a catalytic amount of dilute hydrochloric acid for three hours produced II (9.0 g., 0.05 mole), m.p. 76-77°. Literature reports m.p. 77-77.5° (8).

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Hattiesburg, Mississippi 39401