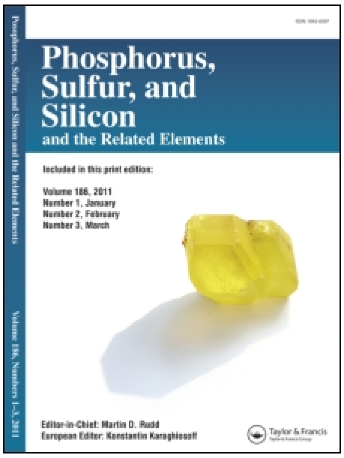

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A Simple One-Pot Synthesis of Methyltribromosilane

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A Simple One-Pot Synthesis of Methyltribromosilane

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A simple one-pot synthesis of methyltribromosilane has been developed. The straightforward reaction of a slight excess of silicon tetrabromide with one equivalent of powdered methyllithium in refluxing pentane produces methyltribromosilane in high yields.

Keywords Halogenated organosilanes; methyltribromosilane; Rochow synthesis; silicon carbide

INTRODUCTION

Halogenated organosilanes are today used in an enormous variety of industries and in a diverse array of applications. Methyltribromosilane and other halogenated organosilanes are of interest as precursors for the Chemical Vapor Deposition (CVD) of β-SiC films,[1,2] and in the synthesis of novel polysilyne network polymers.[3–5] Methyltribromosilane and other halogenated organosilanes are usually prepared by the Rochow synthesis,[6] or by a method involving dropwise addition of a Grignard reagent to an ether solution containing silicon tetrabromide.[7] The former method requires high temperatures and the use of hydrogen bromide gas, and the later synthesis is complicated by difficult separation of the products. In this article, we report a simple, alternative route to the production of methyltribromosilane.

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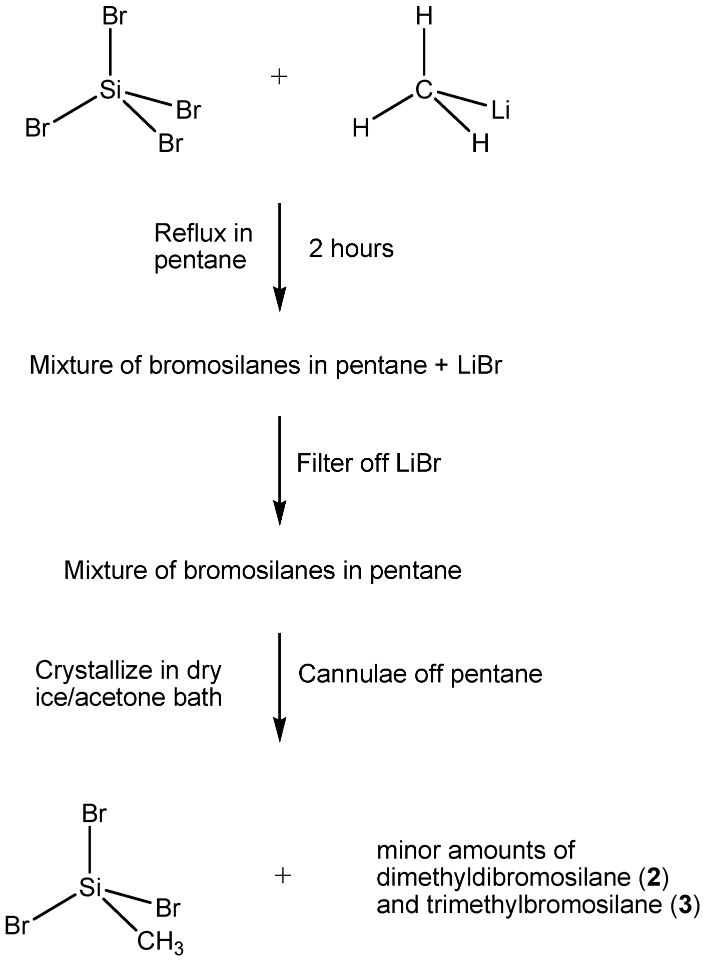
RESULTS AND DISCUSSION

The simple addition of powdered methyllithium to a refluxing mixture of silicon tetrabromide and pentane produces white crystalline bromosilane products which are easily isolated. NMR studies of the crystalline material confirm the major product to be methyltribromosilane (**1**—Scheme 1), along with smaller quantities of dimethyldibromosilane



1

methytribromosilane

SCHEME 1

($(CH_3)_2SiBr_2$) (**2**) and trimethylbromosilane ($(CH_3)_3SiBr$) (**3**).[8] ^1H NMR (200 MHz, d_6-benzene) shows the methyl resonance of **1** at $\delta = 1.00$, that of **2** at $\delta = 0.67$, and that of **3** at $\delta = .31$, in a ratio of 4.1:1.9:0.5 by integration. ^{13}C NMR (75.5 MHz) shows a methyl resonance at $\delta = 126.6$ (triplet, $J_{C-H} = 96.4$ Hz) corresponding to methyltribromosilane (**1**). The other resonances at $\delta = 124.2$ (triplet) and $\delta = 121.4$ (triplet), corresponding to the methyl groups of the di-and tri-methyl-substituted products are not seen. Elemental analyses: Found (C 5.03%, H 0.91%); Calculated for (CH_3SiBr_3) (C 4.24%, H 1.06%). Based on the ^1H NMR, the reaction product therefore consists of 79% CH_3SiBr_3, 18% $(CH_3)_2SiBr_2$ and 3% $(CH_3)_3SiBr$. The purity is acceptable, for the intended use as a reagent in the synthesis of poly(methlysilyne).[3] Fractional distillation of the mixture, would enable isolation of pure methyltribromosilane.[6,7] Although this process has not been used to produce any other halogenated organosilanes, it is presumed that this facile synthesis method could be used as a route for the preparation of these compounds, too.

EXPERIMENTAL

Silicon tetrabromide (99+%) was purchased from Aldrich and used as received. Methyllithium in diethylether (1.4 M) was purchased from Aldrich; the ether was removed by vacuum and the methyllithium used in powder form. Anhydrous pentane (99+%) was purchased from Aldrich and dried over sodium and benzophenone. All work was performed under an argon atmosphere, using either a glove box or schlenk line techniques.

Using a two-necked 300 ml round bottom flask equipped with a stirrer, reflux condenser and powder addition funnel, addition of powdered methyllithium (3 g, 0.1367 mol) to a 5% excess of silicon tetrabromide (50 g, 0.1438 mol) in 250 ml of pentane, was done at a rate sufficient to maintain reflux (about a one-hour addition time, Scheme 1). The reaction mixture was then refluxed for an additional hour in order to ensure complete reaction.

After reflux, the apparatus and products of the synthesis were allowed to cool to room temperature, and the lithium bromide side product was removed by filtration. The bromosilane reaction products can then be isolated from the remaining pentane by crystallization in a dry-ice/acetone bath. After immersion for approximately two hours, the pentane can be cannulaed off, leaving white crystals (28.1 g, 69.1% yield based on methlytribromosilane) behind.

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